SORPTION, DEGRADATION AND MOVEMENT OF ATRAZINE AND METOLACHLOR IN SOME MALAWI SOILS

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DECLARATION

I, Deliwe Dinah Lakudzala (Nee Nkhoma), declare that this is my own work and that it has not been presented or submitted elsewhere for any award. All additional sources of information used have been acknowledged.

Deliwe D. Lakudzala Date

CERTIFICATE OF APPROVAL

We hereby declare that this thesis is from the students' own effort and where assistance has been sought, this has been duly acknowledged. It has, therefore, been submitted this day with our approval.

Professor John D. K. Saka	Date
Associate Professor Wellington R. L. Masamba	Date
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ABSTRACT

This thesis concerns aqueous batch–type adsorption studies, laboratory degradation studies and laboratory packed soil column and field leaching studies which were conducted to determine the influence of soil properties on retention, degradation and mobility of atrazine and metolachlor in Ngabu clay, Thyolo clay, Makoka sandy clay loam, Bvumbwe loamy sand and Chancellor College sandy loam. A snapshot survey was also conducted to assess ground and surface water contamination by atrazine and metolachlor in the Zomba/Bvumbwe region. No herbicide residue was detected in the groundwater samples. In surface water samples atrazine was detected in 38% and metolachlor was detected in 15% of the samples. The concentrations of the herbicides were at their highest soon after the first run off event after herbicide application. The concentrations, however were generally below the World Health Organization's (WHO's) recommended maximum guideline values. Following the first run off event concentrations of herbicides steadily decreased with time, decreasing to zero within eight weeks of herbicide application at 37% of the water sampling points that had herbicide contamination. Light soaking rains, higher clay content, flat land, longer distance between agricultural land and surface water body (filtering area), lower herbicide application rates and herbicide incorporation seemed to reduce herbicide export to surface water.

The L-type and C-type sorption isotherms were observed for atrazine and metolachlor on all soils, such that the adsorption of atrazine and metolachlor are described well by Freundlich (r^2 = 0.96 to 0.99), Linear (r^2 = 0.90 to 0.990, Langmuir (r^2 = 0.80 to 0.96) and Temkin (r^2 = 0.94 to 0.99) isotherms. The atrazine and metolachlor adsorption conformed to the isotherms in the following order: Freundlich > Temkin > Linear > Langmuir. The adsorption coefficients (k_d), at 25^0C, of both herbicides were related to soil organic carbon content (r = 0.88** for atrazine and r = 0.99*** for metolachlor) and cation exchange capacity (r = 0.98*** for atrazine and r = 0.89** for metolachlor). The k_d for atrazine was also related to clay content (r = 0.81*).

After the first 24-hour desorption period, the amounts of herbicide desorbed from the Bvumbwe, Chancellor College, Makoka, Ngabu and Thyolo soils ranged from 10-40, 4-22, 12-27, 0.75 -10 and 3-25 %, respectively, of the herbicide that had adsorbed. The degree of desorption depended on type of soil and the initial concentration of herbicide. Desorption was hysteric in all cases, being more irreversible at the lowest herbicide concentrations adsorbed.

Desorption was inversely related with organic carbon (r^2 = -0.85 for metolachlor and -0.75 for atrazine), clay (r^2 = -0.78 for metolachlor and -0.64 for atrazine) and cation exchange capacity (r^2 = -0.91 for metolachlor and -0.74 for atrazine). Thus the Ngabu soil with highest organic matter and high clay content had least desorption whereas the Bvumbwe soil with lowest organic matter and clay contents had the most desorption.

Degradation of the two herbicides was initially fast and then followed by a slow degradation process. The degradation of atrazine and metolachlor was described well by simple first order (SFO), bi exponential (DFOP) and hockey stick (HS) kinetic models (r^2 = 0.95 - 0.99, 0.97 - 0.99 and 0.91 – 0.99, respectively). Atrazine and metolachlor degradation conformed to the kinetic models in the following order: DFOP>SFO>HS. The half –lives for SFO model varied from 25 - 45 days for atrazine and 28 - 58 days for metolachlor, and were significantly correlated with adsorption coefficients (r^2= 0.99 for atrazine and r^2 = 0.87 for metolachlor), and clay (r^2= 0.88 for atrazine and r^2 = 0.92 for metolachlor) and organic matter contents (r^2= 0.83 for atrazine and r^2 = 0.77 for metolachlor) of the soils.

The mobility of herbicides was affected by the intensity of herbicide adsorption by soil constituents (k_d), solubility of the herbicide in water, initial soil water content at the time of herbicide application, the level of water input after herbicide application and herbicide longevity (half life). The leaching of herbicides was inversely related to soil k_d (r^2 = - 0.99*** for atrazine and r^2 = - 0.91*** for metolachlor). Horizontal movement of atrazine was affected by soil texture and amount and timing of rainfall. Mobility index (MI) values showed that leaching of the two herbicides followed the order Bvumbwe>Chancellor College>Makoka>Thyolo>Ngabu. This order was confirmed by the groundwater contamination potential (GWCP) ratings derived using the simple decision aid model.

These results indicate that export of herbicides to water bodies can be reduced by maintaining high organic matter in soils, not applying herbicides when soil is too wet or too dry, following recommended land husbandry practices that reduce soil erosion and maintaining a percentage of the agricultural land as a filtering zone. The results also show that recommendations on application rates for herbicides should consider the clay mineralogy of the soil in addition to type of weeds, crop and clay content of the soil.

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ACRONYMS AND ABBREVIATIONS

AOAC	Association of Official Analytical Chemists
APHA	American Public Health Association
Al	Aluminium
AR	Analytical Reagent grade
ARET	Agricultural Research and Extension Trust
B	Boron
BET	Brunauer, Emmet and Teller's
Ca	Calcium
CAC/PR	Codex Alimentarius Commission/Pesticide Residue
Chanco	Chancellor College
CDPR	California Department of Pesticide Regulation
CEC	Cation exchange capacity
cm	Centimetre
Cu	Copper
DFOP	Bi exponential kinetic model
DT_{50}	Time observed for 50% of the applied herbicide to dissipate.
D%	Desorbed amounts, as percentages of amounts adsorbed
EC	Emulsifiable concentrate
EMWG	Exposure Modelling Work Group
EPA	Environmental Protection Agency
ESA	Ethane sulphonic acid
EU	European Union
EWG	Environmental Working Group
EXTOXNET	Extension Toxicology Network
FAO	Food and Agricultural Organization
Fe	Iron
FOCUS	Forum for the Co-ordination of pesticide fate models and their Use
FOMC	Gustafson and Holden kinetic model
g	Gram
GC	Gas Chromatograph
GLEAMS	Groundwater Loading Effects of Agricultural Management Systems / (practices)

GWCP	Ground Water Contamination Potential
Ha	Hectare
Hr	Hour
HLP	Herbicide Leaching Potential
HPLC	High Performance liquid Chromatograph
HS	Hockey Stick kinetic model
K	Potassium
k_d	Sorption (adsorption) coefficient
k_f	Sorption (adsorption) capacity
kg	Kilogram
k_{oc}	Partition coefficient normalized with respect to carbon content
k_{ow}	Measure of the tendency of a solute to dissolve from water into immiscible 1-octanol
L or l	Litre
LC	Liquid chromatograph
LD_{50}	Lethal dose for fifty percent of the organisms
$LSD_{0.05}$	Least Significant Difference(s) at 5 percent level
M	Moles per litre
MACRO	Pesticide Fate in Macro porous Soil
MBS	Malawi Bureau of Standards
MCL	Maximum concentration limit
Mg	Magnesium
MI	Mobility index
ml	Millilitre
mm	Millimetre
Mn	Manganese
Mw	Malawi
N	Nitrogen
Na	Sodium
NICA	Non ideal competitive adsorption model
NIOSH	National Institute for Occupational Safety and Health
ng	Nanogram
OA	Oxanilic acid
OC	Organic carbon

OCHA	Office for the Coordination of Humanitarian Affairs
OECD	Organization for Economic Cooperation and Development
OH	Hydroxyl
OM	Organic matter
OSHA	Occupational Safety Health Administration
P	Phosphorus
p	Probability
PEARL	Pesticide Emission Assessment at Regional and Local scales
PCB	Pesticide Control Board
PELMO	Pesticide Leaching Model
PESTLA	Pesticide Leach and Accumulation Model
pH	$-\log_{10} [H^+]$
ppb	Parts per billion
ppm	Parts per million
PRZM	Pesticide Root Zone Model
RZWQM	Root Zone Water Quality Model
RSD	Relative standard deviation
SADC	Southern African Development Committee
SC	suspension concentrate
SFO	Simple First Order kinetic model
SLP	Soil Leaching Potential
TLC	Thin Layer Chromatography
UN	United Nations
UNIMA	University of Malawi
US	United States
USA	United States of America
USDA	United States Development Agency.
US EPA	United States Environmental Protection Agency
WG	Wettable granules
WHO	World Health Organization.
WP	Wettable powder
WSSA	Weed Science Society of America
Zn	Zinc

CHAPTER 1: INTRODUCTION

1.1 Background

Pesticides have improved the quality of life by controlling insects that transmit diseases or damage property and increasing crop and animal production. Although there are many benefits from the use of pesticides, the misuse of pesticides can cause both environmental pollution and economic losses. There is concern that pesticide misuse may contaminate agricultural products as well as surface and groundwater and have adverse impacts on public health and wildlife. To protect human health and the environment, the Stockholm Convention (Stockholm Convention, 2001), a global treaty on persistent organic pollutants, was adopted in 2001. The Stockholm Convention bans or severely restricts the use of persistent organic pollutants (chemicals that remain intact in the environment for long periods of time, are widely distributed geographically, accumulate in fatty tissue of living organisms and are toxic to humans and wildlife). The persistent pesticides are DDT, aldrin, dieldrin, endrin, chlordane, heptachlor, hexachlorobenzene, mirex and toxaphene. Less persistent pesticides are currently being used although these also contaminate the environment. They have been found in water and air at levels that give cause for concern in spite of the relatively rapid degradation rates quoted for the compounds (Chapman, 1992; McConnell, 2005). For example, very high levels of atrazine (2-chloro-4-(ethyl amino)-6-isopropylamine-1, 3, 5-triazine) and metolachlor (2-chloro-N-(2-ethyl-6-methyl phenyl-N-(2-methoxy-1-methyl ethyl) acetamide) have been detected in surface and ground waters in temperate regions (US EPA, 2002; EXTOXNET, 2000a and b; Rebich *et al*, 2004; Savoca *et al*, 2000; WHO, 1996; EWG, 2004) and in tropical regions (Lanchote *et al*, 2000; Laabs *et al*, 2002 and Li *et al*, 2001; Du Preez *et al*, 2005)). In the United States of America, from 2000 to 2003, atrazine and metolachlor in air ranged from 0 to 62 and 0 to 78ng/m^3, respectively; in rain they ranged from 0 to 37 and 0 to 55 ng/m^3, respectively, with maximum concentration peaks occurring during herbicide application periods (USGS, 2001)

Atrazine has been reported to have long–term reproductive and endocrine–disrupting effects. Reports have indicated that atrazine disrupts frog development and also causes a variety of adverse effects in fish, including reduced reproduction, kidney damage, disruption of normal behaviour and decreased ability to withstand warm temperatures (Hayes *et al*, 2002; USGS, 2001). Atrazine is also reported to be probably a human carcinogen (Van Leeuwen *et al*, 1999). N-nitrosamines, which may be formed in soils that have been treated with atrazine,

have mutagenic and carcinogenic properties (Ayanaba *et al*, 1973). In addition to health effects, soil atrazine concentrations of at least 10^{-4}M have been reported to inhibit sulphate uptake by crops (Hance, 1980; p 309). Atrazine is banned in some countries (including Angola) and restricted South Africa (Zeljezic *et al*, 2006). The Natural Resources Defence Council filed a petition in 2002 asking the Environmental Protection Agency (EPA) in United States to ban use of atrazine to protect endangered turtles, frogs and mussels and in 2003 sued the EPA for approving use of atrazine without properly considering the effects on endangered species (Heilprin, 2003). According to EXTOXNET (1996) metolachlor has the potential to cause liver damage and irritation of skin, eyes and mucous membranes from a lifetime exposure at levels above the MCL. Signs of human intoxication from metolachlor exposure include abdominal cramps, anaemia, and shortness of breath, dark urine, convulsions, diarrhoea, jaundice, weakness, nausea, sweating and dizziness. However, metolachlor is not carcinogenic or mutagenic.

Individuals may be exposed to atrazine or metolachlor by drinking water from wells or rivers which are contaminated with the herbicides or swimming in herbicide contaminated waters. Farm workers, chemical sprayers and people who work in factories that make the herbicides may also be exposed. Individuals can also be exposed to the herbicides by digging in soil or dirt that contains the herbicide residues. Exposure through food or inhalation is very rare as the herbicide concentrations are low in air and the herbicides are rarely found in food; if found it is only at very low levels (US EPA, 2002).

WHO (1990) estimated that 5-10% of the agricultural population in developing countries are likely to have significant exposure to pesticides leading to pesticide poisoning. According to Saka (1999) the situation could arise due to lack of knowledge on toxicity and harmfulness of pesticides and inadequate knowledge on correct application procedures (to protect oneself and the environment) and dosages that are common in these areas.

1.2 Utilization of pesticides in Malawi

In Malawi, rapid agricultural development has led to an increased use of pesticides. At least 2000 metric tons of pesticides are used annually, 70% of which are used for agriculture. The major crops on which pesticides are used are shown in Table 1 (Kapeya *et al*, 2003). Cotton is

the most pesticide intensive crop. However, the estimated pesticide usage on cotton is lower than that of tobacco, coffee and sugarcane because of the low total hectarage under cotton. More recent data on pesticide use by crops in Malawi is not available (Mtambo, 2007 and Mvula, 2007; *personal communication*).

Table 1: Major crops and pesticide use (Kapeya *et al,* 2003)

Crop	Estimated use (%)
Tobacco	40-50
Coffee	15-20
Sugarcane	10-15
Cotton	10
Tea	5
Maize	4

The pesticides, which include insecticides, herbicides, fungicides, fumigants, and rodenticides, are shown in Table 2 (Kapeya *et al,* 2003). While insecticides are mostly used in field crops, fumigants are mostly used in the tobacco industries and herbicides are mostly used in the sugarcane plantations, coffee, cotton and tobacco fields. The mostly used pesticides are insecticides, followed by herbicides. Quantities of insecticides are large but fluctuate with time, depending on pest or disease outbreaks. For example, imports of insecticides decreased in 1999 and 2006 reflecting less usage in the previous years hence unused stocks which reduced demand. The use of herbicides has steadily increased with time from 1998 to 2006. In 1998 more insecticides than herbicides were used (see Table 2). In the year 2000 more herbicides (a total of 196500 litres plus 126000 Kg) than insecticides (a total of 63000 litres plus 149000 Kg) were used. The increase in use of herbicide is in line with what is happening on the global level. According to Kearney and Kaufman (1975) the production and use of insecticides have remained fairly constant over the last several years but there has been a dramatic increase in the use of herbicides in plant production programs. As the world's demand for food increases, as labour becomes scarce and expensive and as no till or minimum tillage soil conservation practices are implemented, the most rapid rates of

Table 2: Imports of pesticides into Malawi (Kapeya *et al,* 2003)

Item	Quantity							
	1998		1999		2000		2005	2006
	Liquids (l)	Solids (kg)	Liquids (l)	Solids (kg)	Liquids (l)	Solids (kg)	Solids (kg)	Solids (kg)
1.Insectcides								
1. 1 Chlorinated hydrocarbons	2,540		6,700		840			
1.2 Organic-phosphates	15,590	3,600	33,308	54,078	13,512	3,925		
1.3 Carbamate-insecticides						44,000		
1.4 Pyrethroids	1,492	450	3,270		1006			
1.5 Others	11,600	185,521.6	28,482	60,992.5	47,877	100,799		
Total Insecticides	31,222	189,571.6	71,760	63,230	63,230	148,724	1,448,968	1,198,751
Mineral Oils	2,500		976		2,300			
2. Herbicides								
2.1 Phynoxy hormone products	11,195		10,870		99.350			
2.2 Triazines	2,000	14,000	3,400	11,000	7,610	18,000		
2.3 Amides	6,200		3,500		6,000			
2.4 Carbamate-herbicides	3,000		9,000	-	2,500	-		
2.5 Urea derivatives	6,000		2,500		2,500			
2.6 Sulphonyl ureas	150				2,500			
2.7 Bipiridils	47,460		30,820		17,540			
2.8 Others		40,783	10,293	47,015	60,954.6	108,173		
Total Herbicides	113,341	54,783	92,883	58,015	196,454.6	126,173	562,507	570,001
3. Fumigants	25,200	23,525.24	29,900	2,016.24	12,000	16,834.{		
4. Nematicides				16,020		44,000		
5. Fungicides								
5.1 Organic-phosphate		50		50				
5.2 Carbamates		1,005	3,000	801		200		
Total Fungicides		1,055	3,000	851		200	256,863	123,186
Rodenticides		25		25		267	16,287	68,993

expansion in pesticide production will be in the field of herbicides. Hand hoeing is the most common method used to control weeds by small scale farmers in Malawi and this is labour intensive. The impacts of both rural–urban migration and HIV/AIDS are making it increasingly difficult for many families to successfully weed their crops using this method. The Sasakawa Global 2000 Malawi is working with small scale farmers, encouraging them to use herbicides.

1.3 Fate and dynamics of herbicides

While a small proportion of the pesticides applied reach the target species, a considerable amount ends up in soil (Hassall, 1982). The environmental fate of pesticide residues in soil include uptake by plants growing on the soil (hence entering the food chain), biodegradation by micro organisms, translocation into air (through volatilization and wind erosion), run off in surface water, leaching into subsurface water, sorption to soil and soil organic matter, photo degradation by sunlight and chemical degradation. The fate and degree of transport of pesticide residues in the environment depends on several factors such as temperature, moisture, microbial activity, amount of oxygen, sunlight, rainfall patterns, application rate, topography and rainfall (Zaranyika and Mugari, 1996; Kalkhoff *et al*, 2003; Lin *et al*, 1999), physical and chemical properties of the pesticides, soil adsorption, pH, organic matter, clay and soil dissipation half lives (Savoca *et al*, 2000; Stevenson, 1994; Abate *et al*, 2004).

There have been several reports on sorption, persistence and mobility of pesticides in soils in the United States of America (Rice *et al*, 2002; Weber *et al*, 2003 and Singh, 2003), in Greece (Albanis *et al*, 1998), in India (Sanyal *et al*, 2000), in France (Novak *et al*, 2003), in Italy (Francaviglia and Capri, 2000), in Portugal (Cerejeira, 2003), in Brazil (Laabs *et al*, 2002), and in Africa (Osano *et al*, 2003; Wiese and Basson, 1966; Du Preez, 2005). Most studies (77%) on persistence and mobility of pesticides in soils have been on temperate zone conditions, and the majority of reports on tropical zone conditions originated in India (Wandiga, 2001; Racke, 2003).

The dynamics and stability of pesticides in the temperate soils is different from that in the tropical soils. Gupta and Kavadia (1979) found that aldrin degraded faster in Indian soils than in temperate soils. Kollman and Segawa (2000) found metolachlor to have an average half-life of 114 days in temperate soils whilst Sanyal *et al*. (2000) reported a field half life of 27

days in tropical soils of India. There is so much variation in literature of sorption coefficient values, hence degradation and mobility, because of the complexity of soil environments. Extrapolation of soil values from one area to another is therefore not reasonable. No studies have been done on sorption and persistence of pesticide residues in Malawi soils.

As the fate of pesticides in soils is determined by numerous interacting processes (solute transport, degradation, sorption, plant uptake, volatilization and so forth) mathematical models have been developed to understand and to predict pesticide leaching in soils. The REM (Register of Ecological Models) database has several pesticide leaching models (REM, 2000). In addition FOCUS (Forum for the Co–ordination of pesticide fate models and their Use) has recommended models for simulating pesticide leaching (FOCUS, 1996 and FOCUS, 2000a). The FOCUS groundwater group (FOCUS, 2000a) selected PELMO, PRZM-2, MACRO and PESTLA to be used in pesticide registration in the EU. Later PESTLA was replaced by PEARL (FOCUS, 2000b). The quality of simulation results depends on the structure of the model and its parameterization. Highly regarded models for herbicide fate simulations are MACRO 4.1, GLEAMS 3.0, RZWQM, PEARL and PELMO (Siimes and Kamari, 2003). Pesticide leaching models have not been used in Malawi. Use of pesticide leaching models requires determination of sorption coefficients and half lives of each pesticide in each soil.

1.4 Problem statement

There are indications that pesticide contamination in water exists in Malawi. Government water quality tests had identified dangerously high levels of aldrin and dieldrin in Lilongwe River (MEREP, 1995). The aldrin and dieldrin were believed to have come from termite control activities. Kamperewera *et al* (2000) found high levels of aldrin, lindane and some DDT isomers in sediments in Mtemankhokwe stream in Mangochi district. However concentrations of these compounds in the water from Lake Malawi were relatively low (Karrlson *et al*, 2000). Banda (2004) found DDT, aldrin and hexachlorocyclohexane isomers (α-HCH, δ-HCH and γ-HCH) in water in Lunyangwa river basin, and in most cases the pesticides exceeded 100µg/l. He also found that α-HCH, γ-HCH and aldrin were most prevalent in sediments than in the water.

However, no studies have been done to assess herbicide levels in soils and waters of Malawi.

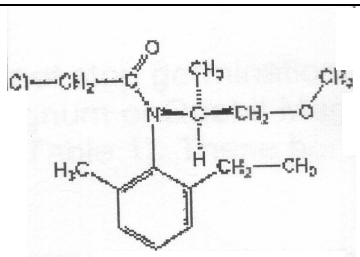
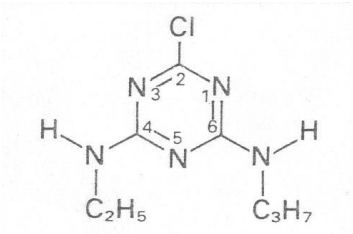
Atrazine and metolachlor were chosen for this study. The herbicides, containing atrazine and metolachlor, registered for use in Malawi are shown in Table 3.

Table 3: Herbicides containing atrazine and metolachlor registered for use in Malawi (Mw PCB, 2007)

Herbicide common name(s)	Trade name	Formulation	Concentration
Acetochlor + Atrazine + Propazine	Tuff-E-Nuff	SC	96g + 202g + 202g/litre
Acetochlor + Atrazine +Simazine	Robust	SC	160g + 165g + 165g/litre
Acetochlor + Atrazine +Terbuthylazine	Acetrazine	SC	125g + 187.5g +187.5g/litre
Atrazine + Terbuthylazine	Suprazine Eliminator	SC SC	600g/litre 500g/litre
Atrazine + Terbuthylazine + Metolachlor	Gadomil	SC	262.5g + 262.5g + 175g/litre
Cyanazine + Atrazine	Blazine Bladex Plus	SC SC	250g + 250g/litre 333g + 167g/litre
Atrazine	Atrazine Gesaprim	SC,WP, WG WG, SC	500g/litre, 800g/kg, 900g/kg 900g/litre, 500g/litre
Atrazine +.Acetochlor + Terbuthylazine	Bullet	EC	225g + 250g + 225g/litre
Pendimethalin + Ametryne + atrazine	Paragon plus	WP	350g + 200g +200g/kg
Metolachlor	Dual magnum Falcon gold Sorgomil gold Metolachlor novachlor	EC EC SC EC EC	960g/litre 960g/litre 600g/litre 960g/litre 960g/litre
Terbuthylazine + Metolachlor	Sorgomil	SC	700g/litre
Terbuthyn + Metolachlor	Igran Combi Trifluralin	SC EC, SC	490g + 10g/litre 480g/litre, 500g/litre
Metolachlor + flumetsulam	Baleleur gold	EC	630g + 20g/litre

Atrazine and metolachlor were chosen firstly because studies conducted in the USA, South Africa and elsewhere on various pesticides have shown that the two are the most common pesticide contaminants in ground and surface waters (US EPA, 2002; EXTOXNET, 2000a and b; Rebich *et al*, 2004; Savoca *et al*, 2000; WHO, 1996; EWG, 2004; Du Preez *et al*, 2005) and secondly because of their use in agricultural practices in Malawi. Atrazine is widely used by smallholder farmers on maize fields (under the Sasakawa Global 2000 Malawi project) and in sugarcane estates whilst metolachlor is widely used on tobacco, cotton and coffee estates. The physical, chemical and other properties of atrazine are shown in Table 4.

Table 4: Identity, physical and chemical properties of metolachlor and atrazine

Property	Metolachlor	Atrazine
Chemical structure		
chemical group	chloroacetanilide	triazine
Chemical formula	C15 H22 ClNO2	C8H14ClN5
Relative molar mass	283.80g	215.69g
IUPAC chemical name	2-chloro-N-(2-ethyl-6-methyl phenyl-N-(2-methoxy-1-methyl ethyl) acetamide	2-chloro-4-(ethyl amino)-6-isopropylamine-1, 3, 5-triazine
Density, g/cm^3	1.12	1.19
Melting point	-62.1^{o}C	171-174^{o}C
vapour pressure	1.3x10^{-5}mmHg (20^{o}C); or 1.7x10^{-3} Pa	2.78x10^{-7}mmHg; or 4x10^{-5} Pa
Solubility in water	530mg/l	30mg/l
Henry's law constant, 25^{o}C	2.44x10^{-8} atm m^3/mol[a]	2.63x10^{-9} atm m^3/mol
Half life (field), days	average of 114[b]	56-154[c]
Hydrolysis half life, days	>200 (30^{o}C,pH 1-9)	90 (pH<3 or pH>11); 10000 (pH 7-9)[d]
k_{ow} at 25^{o}C	794b[e]	3 x10^3

[a] Ciba – Geigy corporation, 1996

[b] Kollman and Segawa, 2000

[c, f, g] Akerblom, 1995

[d] Koch, 1989

[e] Larson and Weber, 1994

Table 4 Identity, physical and chemical properties of metolachlor and atrazine (continuation)		
Average k_{oc}	200	122
Physical state at room temperature	odourless, white powder	odourless, off-white to colourless liquid
Ionization	weakly basic	non-ionisable
MCL for drinking water, US EPA	0.005 mg/l	0.525 mg/l
LD_{50}	2780[f]	2000[g]
Application	post or pre-emergence	pre-emergence or pre-plant
Target weeds	broadleaf and grass weeds	broadleaf, grass weeds and sedges
Herbicidal action[h]	inhibits photosynthetic electron transfer in chloroplasts, acts through roots of germinating weeds and to a lesser extent foliage	inhibits growth by preventing synthesis of essential plant compounds like chlorophyll, proteins and fatty acids, acts through shoots of germinating weeds before they emerge above ground.
Crops on which used[i]	maize, sugarcane, raspberries, sorghum, asparagus, pineapples, roses and fine forest trees	cotton, tobacco, tea, sugarcane, coffee, maize, potatoes, groundnuts, soybeans, sunflower and woody ornamental fields

Information on sorption, degradation and mobility of pesticides in Malawi soils is lacking. This information is needed in order to avoid adverse effects of herbicides on subsequent crops, soil fertility and environment. This study therefore concerned the fate (sorption, degradation and mobility) of atrazine and metolachlor residues in some soils used for cropping in Malawi.

Apart from the environmental concerns some farmers have complained that the recommended herbicide application rates, by the Ministry of Agriculture, are not effective. This study was designed to address this issue as well.

[h , i] SYNGENTA, 2004

1.5 General and specific objectives

The main objective of the study was to investigate sorption, degradation and mobility of atrazine and metolachlor residues in some soils used for cropping in Malawi. The specific objectives of the study were to:

(i) Determine extent and trends of atrazine and metolachlor contamination in some surface and ground waters in Zomba/Bvumbwe region,

(ii) Determine the sorption and mobility of atrazine and metolachlor in soils and factors affecting the sorption and transport modes and

(iii) Determine degradation of metolachlor and atrazine in soils and factors affecting the degradation and

CHAPTER 2: LITERATURE REVIEW

2.1 Atrazine and metolachlor in air

Atrazine and metolachlor are found in the atmosphere. The US Geological surveys' national monitoring study often found atrazine and metolachlor in air and rain at nearly every location tested (USGS, 2001). Atrazine was found in air both near areas where the herbicide was used and in areas where it was not used. In the United States of America, from 2000 to 2003, atrazine and metolachlor in air ranged from 0 to 62 and 0 to 78ng/m^3, respectively; in rain they ranged from 0 to 37 and 0 to 55 ng/m^3, respectively, with maximum concentration peaks occurring during herbicide application periods (McConnell, 2005). Atrazine and metolachlor are lost to the atmosphere through wind drift (during application), soil erosion and volatilization (Hance, 1980). McConnell *et al* (2002) reported that wind erosion (pesticide residue attached to soil particle) plays a role in transporting atrazine and metolachlor into the atmosphere, especially in areas close to intense agricultural activity.

Presence of metolachlor and atrazine in the atmosphere can result in their long–range transport and redeposition, with the outcome being that measurable quantities of such herbicides can be detected far from their point of release. Atrazine and metolachlor in the air may be broken down by reactions with chemicals in the air, or they may adhere to particles such as dust which eventually settle out of the air through dry deposition (ATSDR, 2003) or wet deposition (Anubha *et al*, 2005).

2.2 Atrazine and metolachlor in water

Soil erosion, as wind drift, sediment transport and run off, is a major potential source of pesticide residues in surface waters. Soil pesticide residues that are picked up in a run off event come from a layer possibly as thin as 2-3 mm (Ahuja, 1982). Herbicide run off from agricultural fields has been reduced with vegetative filter strips (Krutz *et al*, 2005).

A survey conducted in 1999 in Mali revealed that pesticides polluted the water of most villages in northern Mali (UN OCHA, 2000). Albanis *et al* (1998) found higher concentrations of pesticides in groundwater in spring, following seasonal applications, which decreased significantly in autumn. Studies conducted in the USA, where there is large scale use of various pesticides, have shown that the most common pesticide contaminants in ground and surface waters are atrazine and metolachlor (U.S.EPA, 2002; EXTOXNET, 2000a and b; Rebich *et al*, 2004; Savoca *et al*, 2000; WHO, 1996; EWG, 2004). The widespread use of atrazine and metolachlor resulted in their detection in shallow ground waters of 20 major hydrologic basins of the United States (Kolpin *et al*, 1998). Environmental Protection

Agency's pesticides in groundwater Database indicates numerous detections of atrazine and metolachlor at concentrations above the recommended maximum concentration limits (0.003mg/l for atrazine and 0.525mg/l for metolachlor) in groundwater in several states (U.S.EPA, 2002; EWG, 2004).

In USA metolachlor concentrations in groundwater usually range from 0.1 to 1 ppb, with an unusual maximum of 138 ppb (EXTOXNET, 2000a)

In a 1997 surface water survey in the USA, metolachlor was detected in 1644 samples from 312 locations in 14 states (EXTOXNET, 2000a). In a 1988 study of ground and surface water in USA metolachlor was found in 2091 of 4161 surface water samples and in 13 of 596 groundwater samples (WHO, 1996).

In Britain there is evidence of the presence of atrazine at concentrations near to the maximum admissible concentration in groundwater (0.0029 mg/l), although the quantitative reliability is uncertain (Hance, 1987). In South Africa values as high as 0.0093 mg/l have been detected in surface waters in corn growing areas and 0.0008 mg/l in non corn growing areas (Du Preez *et al*, 2005) in Western Highveld region.

Groundwater pollution by pesticides has been extensively studied in temperate regions (van der Berg and van der Linden, 1994; Ritter, 1990) where as data from tropical areas is limited. Recent results of Lanchote *et al* (2000) and Li *et al* (2001) showed that the groundwater in the tropics (Brazil and Hawaii) was contaminated with triazines. This underlines the fact that groundwater pollution is of concern in tropical regions too.

2.3 Atrazine and metolachlor in soils

Atrazine and metolachlor residues are common in soils in areas where they are applied (Hance, 1980). Soil bound residues of atrazine and its degradation products were detected in soils nine years after application (Capriel *et al*, 1985; Schiavon, 1988). Bound (non extractable) atrazine residues are mainly located in the soil fractions smaller than 50µm, which also contain 70-90% of total organic carbon as humified organic matter (Barriuso *et al*, 1991). Any soil pesticide residues are potential contaminants of both surface and groundwater.

At the global level several interventions have been made with regard to decontamination of metolachlor contaminated sites. Zero-valent iron has been used to reduce metolachlor concentrations in soils. Comfort *et al* (2001) reported a field-scale remediation of

metolachlor-contaminated spill site using zero-valent iron. Their photo degradation is also of little significance under most field conditions (EXTOXNET, 1996; US EPA, 2002). Run off, leaching and bio-chemical degradation appear to be the principal routes of their loss from the soil.

2.3.1 Volatilization

Volatilization of pesticides depends on vapour pressure, solubility and turbulence within the atmosphere and the earth's surface (Larson and Weber, 1994). Generally very little metolachlor and atrazine are lost to the atmosphere by volatilization, as is predicted by their low Henry's law constants {2.44 x 10^{-8} for metolachlor (Ciba-Geigy Corporation, 1996) and 2.63 x 10^{-9} atm m^3/mol for atrazine (US EPA, 2002)}, and their low vapour pressures {1.3 x 10^{-5} mm Hg for metolachlor (EXTOXNET, 2000a) and 2.78 x 10^{-7} mmHg for atrazine (US EPA, 2002). Rice *et al*. (2002) observed very minimal volatilization of metolachlor from top and sub soils. If metolachlor volatilizes then ninety-five percent of total metolachlor losses from volatilization occur during the first twelve hours from the application time (Prueger *et al*, 1999).

2.3.2 Sorption

The transfer of molecules from solution onto environmental solid phase such as soil mineral or organic matter is referred to as sorption. Sorption includes adsorption (uptake of compound by the surface of a solid) and absorption (diffusion of molecules into the interior of a solid). Sorption kinetics exhibit two phenomena, an immediate rapid sorption followed by a slow sorption process. Presumably initial quick adsorption is a surface phenomenon (explained by easy, rapid, low-energy adsorption on the most accessible sites), followed by a slow migration and diffusion of the compound into the organic matter and soil mineral texture (less accessible sites requiring more energy) (Dehghani *et al*, 2005; Spongberg and Gangliang, 2000). The reverse of the adsorption process is usually called desorption. Desorption behaviour is sometimes different from that corresponding to the adsorption isotherm. There is hysteresis (irreversibility of adsorption). The ratio $\frac{n_a}{n_d}$ is used to describe the hysteretic behaviour of desorption from soils, where n_a and n_d are the Freundlich n constants obtained from the sorption and desorption isotherms, respectively (Morillo *et al*, 2004). Sorption–desorption equilibrium depends on a number of factors, such as temperature, pH, ionic strength, and surface area of solid as well as its physicochemical characteristics (charge distribution and

density), hydrophobicity, particle size and void volume and water content (Larson and Weber, 1994). Consequently, published adsorption coefficients and capacities, k_d and k_{oc} and k_f, respectively, can only be used as average estimates of the actual values.

Atrazine and metolachlor moderately adsorb on many soils. Their average soil adsorption coefficients (k_{oc}) are 122 and 200, respectively (EXTOXNET, 1996 and US EPA, 2002). Soil binding, k_d, values for atrazine and metolachlor are 2.33 – 39.6 ml/g (Abate *et al,* 2004) and 0.1 – 10 ml/g (Weber *et al,* 2003), respectively. Atrazine adsorption decreases as the pH of a soil increases (Shaner and Henry, 2007). The relative affinity of most soils to atrazine is not affected by the presence of metolachlor. Similarly, affinity to metolachlor is not affected by the presence of atrazine in most soils (Dozier *et al,* 2002). The percentage of applied metolachlor bound to soils decreases with increasing metolachlor application rates (Rice *et al,* 2002). Several isotherms such as linear, Freundlich, Langmuir and Temkin (Zhu and Selim, 2002; Dehghani *et al,* 2005) have been used to quantitatively describe herbicide adsorption to soils. The Freundlich isotherm has been reported to give best fits for both atrazine and metolachlor adsorption data in most soils (Abate *et al,* 2004 and Weber *et al,* 2003).

L-type and S-type sorption isotherms resulted when metolachlor was adsorbed by Ca-organic matter and Ca-montmorillonite (Strek and Weber, 1982; Weber and Peter, 1982 and Liu *et al,* 2002), respectively. L-type or C-type isotherms resulted when metolachlor and atrazine were adsorbed on soils depending on OM/clay ratio (Weber *et al*, 2003).

Desorption of atrazine is positively correlated to the amount of applied atrazine and to the equilibration time and it exhibits hysteretic phenomena (Dehghani *et al*, 2005).

Adsorption–desorption of herbicides to soil components are key processes that can control several other factors such as leaching, degradation and herbicidal activity. Since sorption coefficient characterizes soil/water partitioning it can also be representative for leaching.

The retention of atrazine and metolachlor has been attributed to organic matter and clay (Weber *et al,* 1969; Peter and Weber, 1985; and Zhu and Selim, 2000).

2.3.2.1 Clay mineral adsorbents

In soils the adsorbents are clay minerals and organic matter. Soil retention of atrazine and metolachlor is directly related to organic matter (Weber *et al*, 2003 and Abate *et al*, 2004) and organic matter (OM) and clay content (Rice *et al*, 2002). Clay minerals are very organized,

often forming stacked layers of parallel planes made up of silica tetrahedral and alumina octahedral sheets (Figure 1) (Burton *et al*, 1994).

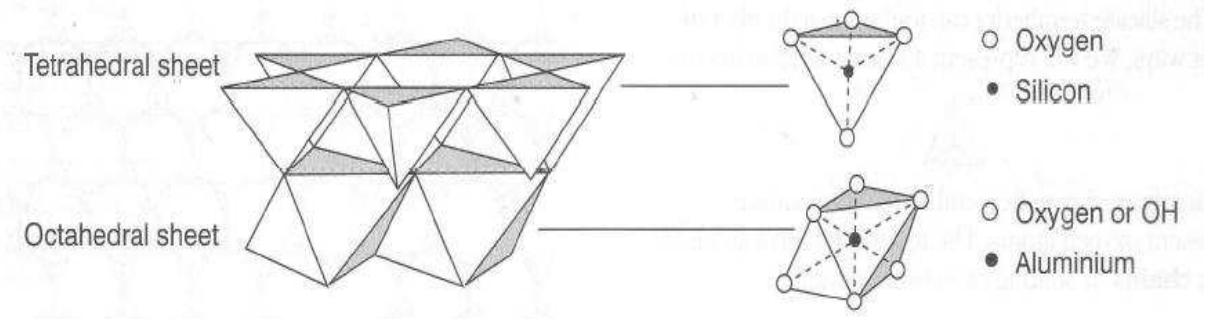


Figure 1: Sheet structure of clay minerals

Clays are classified into 1:1 or 2:1 and occasionally 2:1:1 type clays based on the arrangement of the alumina and silica sheets. A layer of 1:1 type clay mineral is made up of one tetrahedral silica sheet and one octahedral alumina sheet (Figure 2) (Burton *et al*, 1994). Kaolinite is an example of 1:1 type clay mineral.

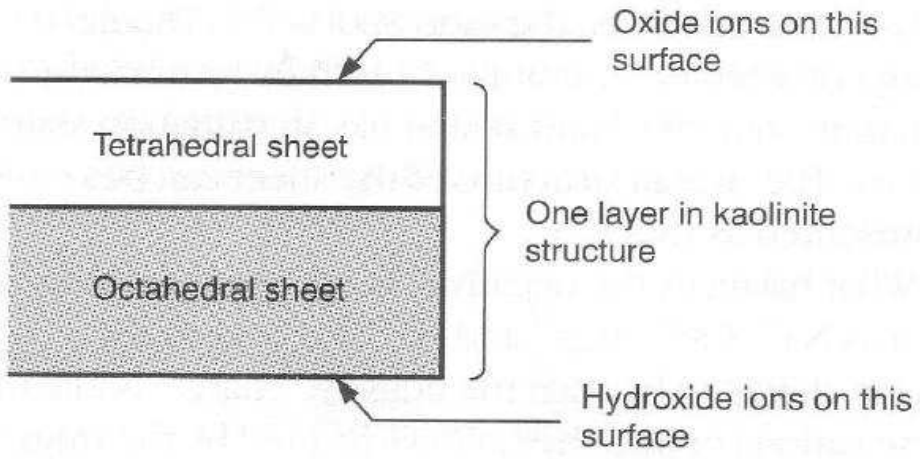


Figure 2: Layer of 1:1 clay mineral

The 1:1 layers in a crystal are held together by hydrogen bonds between hydroxide ions on surface of the octahedral sheet and the oxide ions on the tetrahedral sheet in the next layer (Figure 3) (Burton *et al*, 1994). Water and cations cannot enter between the layers of the crystal and this makes kaolinite a non-expanding mineral.

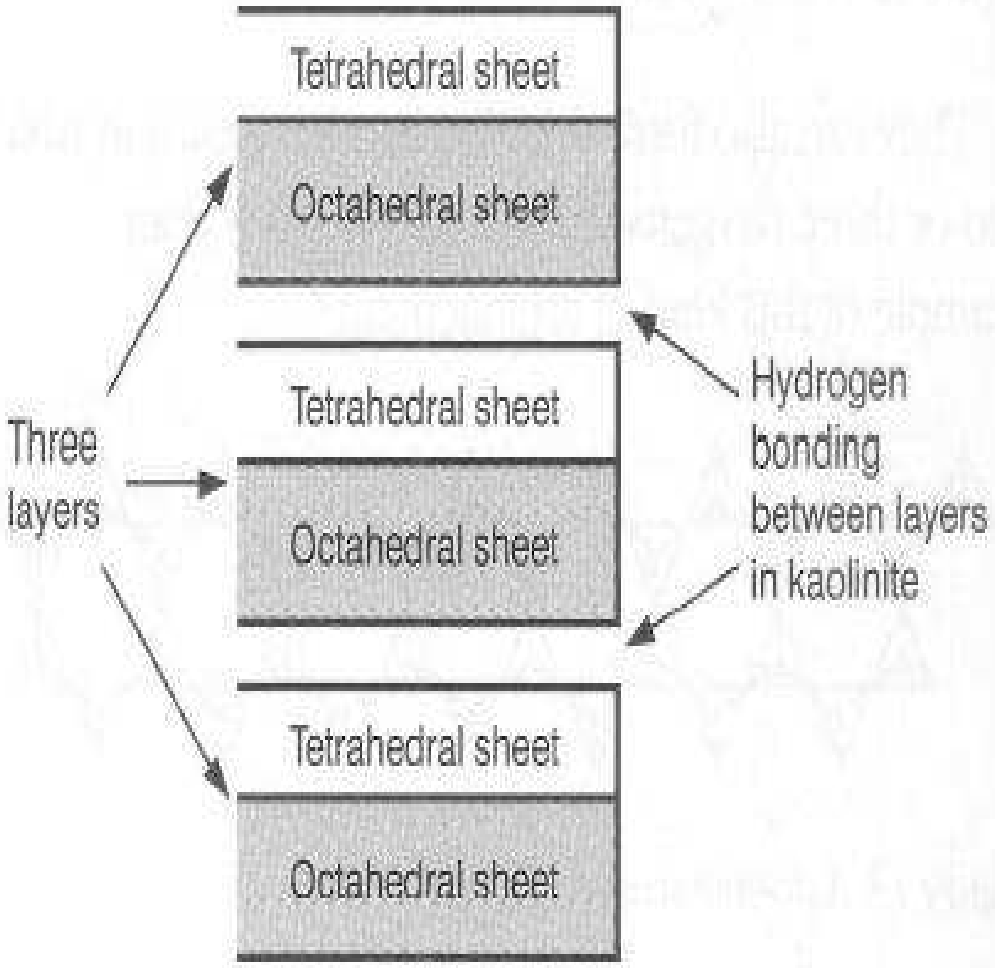


Figure 3: Hydrogen bonding between the layers in kaolinite

In 2:1 type clay minerals an octahedral sheet is sandwiched between two tetrahedral sheets (Figure 4) (Burton *et al*, 1994).

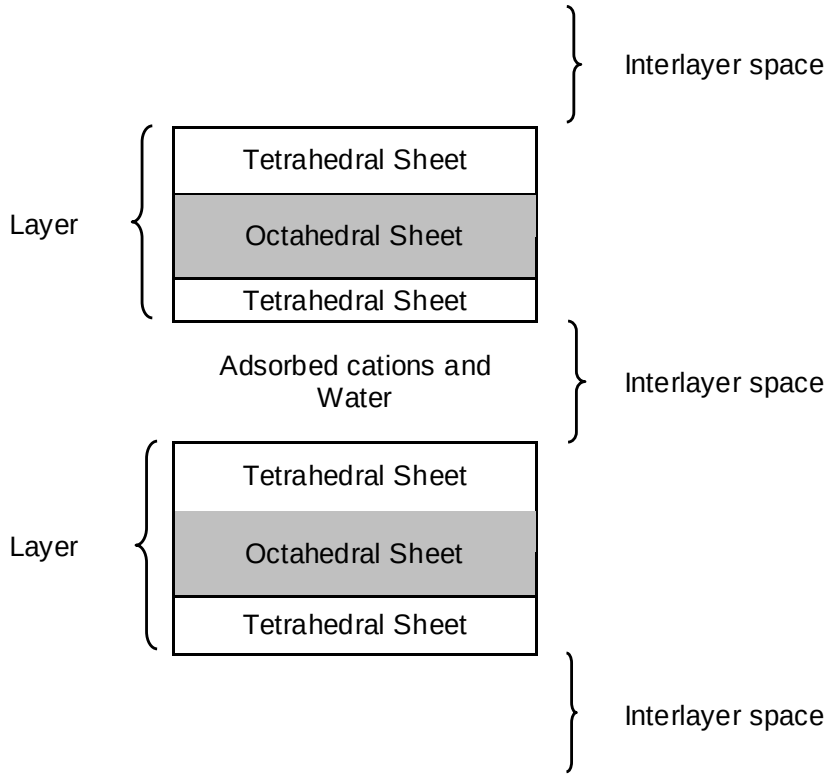


Figure 4: Layers of 2:1 clay mineral

There is little attraction between the oxygens at the bottom of the layer and those at the top of the next layer. This means that water and cations can easily enter the interlayer space in 2:1 type clay minerals. When water enters the interlayer space in a clay mineral it forces the layers apart and exposes a large internal surface. This interlayer surface is much greater than the external surface area of the crystal (Burton *et al*, 1994). The 2:1 type clay minerals are expanding minerals.

The 2:1:1 (also called 2:2) type clay minerals have two silica tetrahedral sheets, one alumina octahedral and one magnesium hydroxyl octahedral sheets. These are considered as 2:1 layer plus an interlayer magnesium hydroxide sheet (Bailey, 1980). The magnesium octahedral sheet is held in the interlayer because aluminium (trivalent) isomorphically substitutes for magnesium (divalent). This gives rise to a net positive charge on the interlayer octahedral sheet Therefore, the platelets are held together electrostatically and this means a 2:1:1 type clay mineral is a non expanding mineral. 2:1:1 type clay minerals are found in acid soils and in ultisols with 2:1 minerals. A good example of 2:1:1 type clay minerals is chlorite.

Clay minerals are extremely fine particles often with diameters of less than 2 µm, and have a high relative surface area. Soils with 2:1 clay minerals have greater adsorption capacity for herbicides than those with 1:1 clay minerals (Herwig *et al*, 2001). Soils with 2:1:1 type clay minerals have properties in between those with 2:1 and 1:1 clay minerals.

In some clays Al (111) and P (111) can partially replace silicon (1V) in the silicate layers and Mg (11), Fe (11) and Zn (11) can substitute for Al (111) in the octahedral layer resulting in a net negative charge on the clay mineral. To achieve electrical neutrality, cations (organic and inorganic) adsorb on the clay surface or to the interlayer spaces (Figure 5). This leads to the possibility of cation–exchange displacement reactions. 2:1 minerals have high cation exchange capacity (CEC). In 2:1:1 clay minerals the positively charged interlayer magnesium octahedral sheet blocks the exchange sites and reduces CEC.

In soils or waters with few alkali or alkaline earth ions the cations on the clay may be protons, making it possible for the surface of the clay to be strongly acidic. Such acidity can enhance the ionization of many compounds such as phenols and anilines. In addition to proton–donating acidity, clays may also possess Lewis acid (electron accepting) sites by virtue of their content of reducible transition metal cations such as Fe^{3+} and Cu^{2+}.

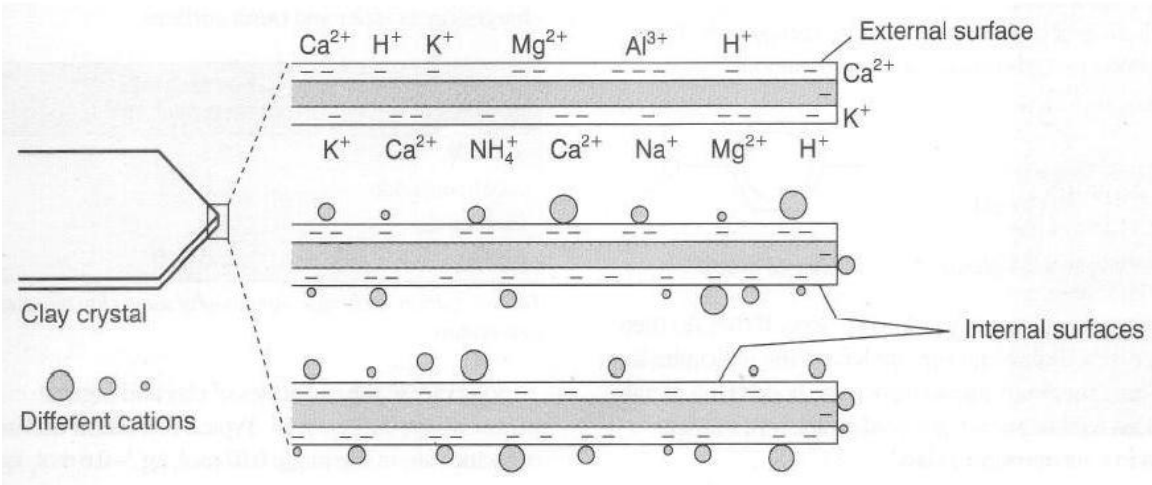


Figure 5: Exchangeable cations at the inner and outer surface of a crystal of a 2:1 clay mineral like montmorillonite

2.3.2.2 Organic matter adsorbents

Soil retention of atrazine and metolachlor is directly related to organic matter (Weber *et al*, 2003; Abate *et al*, 2004 and Rice *et al*, 2002). Soil organic matter is made of plant debris, animal remains and excreta, and the product (such as humus) formed by decomposition of all these things. Humus in soils is either polymeric or strongly bound to soil particles. Humus has many macromolecules with masses up to 500000 g/mol. Ten percent of humus in soil is carbohydrates (sugars and polysaccharides) and virtually all of it is polymeric, but some free monosaccharides have been identified (Larson and Weber, 1994). According to Burton *et al* (1994) major components of humus are esters of carboxylic acids, carboxylic acid derivatives of benzene and phenolic compounds. The carboxylic and phenolic groups can hydrogen bond to organic chemicals or they can lose hydrogen ions, hence become negatively charged, and hold a variety of ions in a similar way to clays. Humus also possesses Lewis acids (electron accepting) sites by virtue of their content of ammonium and reducible transition metal cations. Other functional groups in humus include enolic OH, quinone, hydroxyquinone, lactone, ether and alcoholic OH (Larson and Weber, 1994). Because soil organic matter is so highly oxidized, current thinking is that it must have extensive non-polar regions, perhaps alkyl chains or aromatic branches, which are responsible for the partitioning of organic molecules (Larson and Weber, 1994). The electric concept of humic material is shown in Figure 6 (Gjessings, 1976).

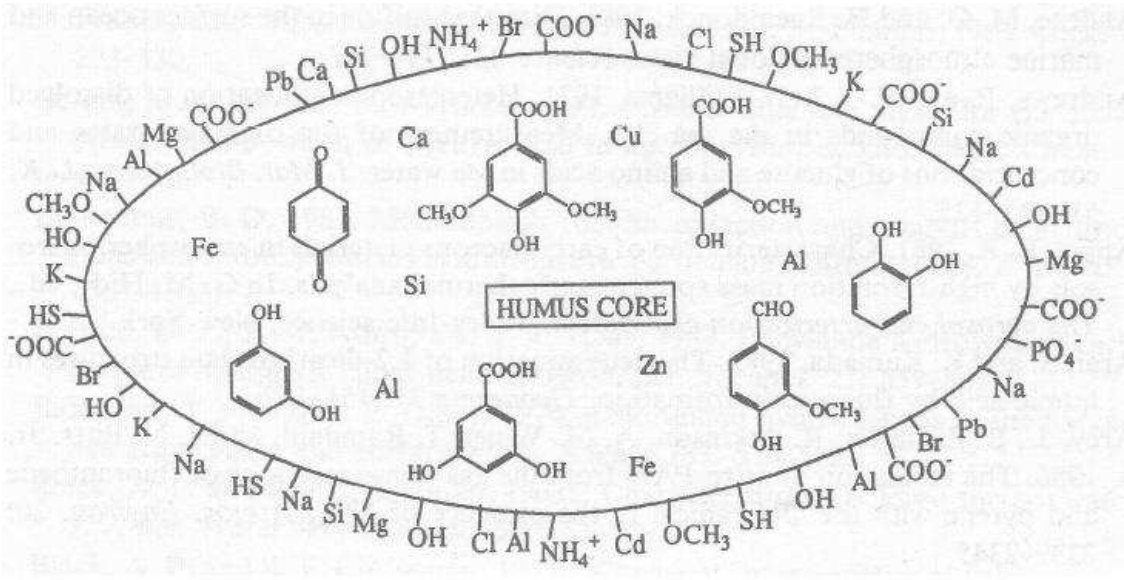


Figure 6: Electric concept of humic material

2.3.2.3 Mechanism of bonding

Clay minerals can interact with organic compounds by adsorption, intercalation (in which the molecules enter the inter layer space and deform the silicate layer), and ion exchange processes (Larson and Weber, 1994). Solute sorption by organic matter can be via surface adsorption or intra organic matter diffusion or ion exchange processes (Pignatello and Xing, 1996; Larson and Weber, 1994).

Association between organic molecules and solid phases include coulombic (electrostatic) interactions and hydrophobic interactions in which non polar organic molecules are attracted into the solid phase. Hydrophobic bonds occur between the aromatic and alkyl side chain of organic molecules and hydrophobic nanosites located between charge sites on colloid surfaces (Laird and Fleming, 1999). The k_{oc} can be used to assess the role of hydrophobic bonds on adsorption of herbicides on organic matter of soils. When hydrophobic bonds are responsible for adsorption of an herbicide on organic matter of soils k_{oc} values are relatively constant among different soils (Morillo *et al*, 2004).

The electrostatic interactions are usually Van der Waals forces, ion–ion and ion–dipole attractions, hydrogen bonding and formation of coordination complexes. Polar organic compounds can hydrogen bond to polar components of organic matter. Polar organic compounds can also hydrogen bond to clay or organic matter surfaces through bridging water molecules. Water molecules in the vanity of certain clays or organic matter are oriented, because of the lone pairs of electrons on the oxygen atom of the water and the positive charges on cations at the clay or organic matter surface. This makes an excess of H atoms to face out into soil solution, and in the presence of compounds with lone pairs of electrons on atoms (such as N or O in atrazine or metolachlor), hydrogen bonding can occur (Figure 7).

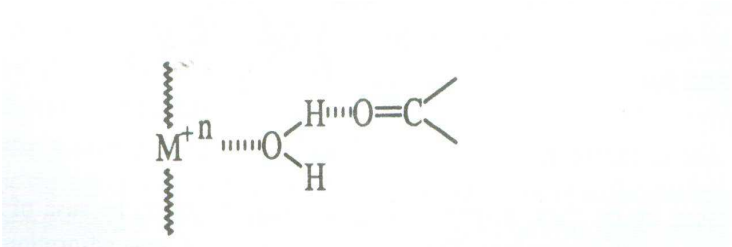


Figure 7: A water bridge, showing how hydrogen bonding may assist in bringing certain organic molecules into the vicinity of clay surfaces

Hydrophobically, bound adsorbates are most strongly bound, followed by cationic adsorbates and lastly anionic adsorbates (Larson and Weber, 1994). Adsorbate–adsorbent bonds belong to two categories: (i) high energy (>80kJ/mole) ionic bonds (permanent charges, such as adsorption of positively charged paraquat on negatively charged clay surface; or ionization, such as protonation of weak bases like atrazine at low pH) and (ii) low energy (<80kJ/mole) bonds such as ion-dipole and dipole-dipole interactions, hydrogen bonds and London van der Waals bonds (Hance, 1980).

2.3.2.4 Sorption isotherms

Isotherms have been used to quantitatively describe pesticide sorption by soils. The isotherms differ in complexity from linear k_d (the simplest) to NICA (the most complex). They range from the relatively simple Langmuir isotherm to single–site adsorption models, multisite adsorption models and porous double layer models. The Linear isotherm, as the name implies, assumes a linear relationship between the aqueous concentration of adsorbate and its adsorbed concentration.

The Langmuir isotherm, originally developed for gas adsorption, has a defined adsorption maximum but assumes linear adsorption at concentrations far below this maximum. It is relatively simple and is based on three assumptions: (i) adsorption cannot proceed beyond monolayer coverage, (ii) all surface sites are equivalent and can accommodate, at most, one adsorbed molecule and (iii) the ability of a molecule to adsorb at a given site is independent of the occupation of neighbouring sites. These assumptions may not be true for heterogeneous adsorbents such as soils (TAU, 2002).

The Freundlich isotherm (Ryan, 2006), used to estimate adsorption at a heterogeneous surface, is also simple but it assumes a non–linear relationship between adsorbed amount and the amount in solution. It does not imply a finite density of adsorption sites. The Temkin isotherm (Ryan, 2006) is similar to Freundlich in scope, but uses a different function to express the non linearity of adsorption. All the abovementioned isotherms have been used to model herbicide adsorption on to soils (Zhu and Selim, 2002; Dehghani *et al*, 2005.). More complicated models, with a large number of parameters and with better goodness of fit, such as the two-term Langmuir isotherm and the BET isotherm, which allow for multilayer

adsorption (the initial adsorbed layer can act as a substrate for further adsorption), have also been used (Fuleky–Tolner, 2006). The goodness of fit, for the complicated isotherms, could readily be attributed to flexibility gained by the increase in the number of parameters. However, these isotherms entail high costs to collect input data. The equations for the isotherms are as follows:

Linear $c_s = k_{dl}\, c_e$, (s_1)

Freundlich $c_s = k_f\, c_e^{\,n}$ or $\log c_s = \log k_f + n \log c_e$ (s_2)

Langmuir $c_s = \dfrac{c_m k_1 c_e}{1 + k_1 c_e}$ or $\dfrac{c_e}{c_s} = \dfrac{1}{k_1 c_m} + \dfrac{c_e}{c_m}$ (s_3)

Temkin $c_s = k_2 + k_t \ln c_e$ and (s_4)

BET $c_s \approx \dfrac{yz}{\{1-(1-y)z\}(1-z)}$ where $z = \dfrac{p}{p+}$ and $y = e^{\frac{(\Delta_{des}H - \Delta_{vap}H)}{RT}}$ (s_5)

where c_s = μmol/kg herbicide adsorbed to soil, c_e = μmo1/l herbicide in equilibrium solution, c_m = maximum μg/g herbicide adsorbed to soil, and $k_{dl,}$ k_f , k_l and k_t, are linear, Freundlich, Langmuir and Temkin sorption coefficients, ml/g, respectively; k_2 is the adjustable Temkin sorption constant, n = linearity factor; p+ is the saturation pressure of the gas (i.e., vapour pressure of the liquid at that temperature), p is the vapour pressure of the gas, y is a constant, $\Delta_{des}H$ is enthalpy of desorption from monolayer and $\Delta_{vap}H$ is enthalpy of vaporization of the liquid adsorbate.

The fitness of the isotherms to sorption data has been determined by plotting the linearized form of the isotherm equations. The conformity of adsorption data for soils to the isotherms is indicated by the coefficient of determination (r^2). The fitness of data to the Langmuir isotherm is tested by plotting $\dfrac{c_e}{c_s}$ against c_e, which should give a straight line with slope $= \dfrac{1}{c_m}$. Maximum sorption (c_m) and sorption coefficient (k_l) are obtained from the plot (Olsen and Watanabe, 1957). The fit of data to Freundlich equation is tested in terms of linearity of log c_s against log c_e plots (Bohn *et al*, 1985). The adsorption constant (k_f) and n can be obtained from the plot. Adsorption models generally used to describe adsorption processes do not assume the presence of any material originally bound on the adsorbent surface, so their starting point is a state with a zero quantity adsorbed material on the adsorbent in a solution with an initial equilibrium concentration of zero.

The choice of isotherm is based on the goodness of fit and the simplicity of the isotherm. As this is the first attempt to model herbicide adsorption, Langmuir and Freundlich isotherms were applied as these are implicitly single site isotherms that do not require an electrostatic term to correct for surface potential. The other reason for choosing Freundlich is because the Freundlich n is needed for pesticide leaching models, such as PELMO. The Freundlich isotherm has been reported to give better fits for both atrazine and metolachlor sorption data than the Langmuir isotherm although it is not able to estimate maximum adsorption capacity as the Langmuir isotherm does (Abate *et al*, 2004 and Weber *et al*, 2003). No general rules have been proposed to describe univocally the relation between the shape of adsorption isotherms and the nature of adsorbate (Calvet, 1989).

2.3.3 Mobility of herbicides

Herbicide leaching is affected by solubility and longevity of the chemical, vegetative cover, type of soil, rate of herbicide application, amount and intensity of water input, soil temperature, processes (such as volatilization and degradation) and pronounced preferential flow transport (Hance, 1980). Mobility is a function of the intensity with which an herbicide is adsorbed by soil constituents and the level of rainfall after herbicide application. Rainfall or irrigation patterns (timing/intensity of rainfall or irrigation) also influence herbicide movement in or from soil (Zaranyika and Mugari, 1996). Light rains increase infiltration and reduce export of herbicides to surface waters. However, very light rains following herbicide application to soils may reduce the effectiveness of the herbicides with solubilities in the range of 1-100ppm (Hassall, 1982), such as atrazine. If rainfall is light, wash down may be insufficient to bring the atrazine into contact with even shallow-rooted weeds hence greatly reducing herbicidal activity. Herbicide incorporation may be advantageous in such cases. On the other hand, if rainfall is excessive, even nearly insoluble herbicides may be washed down to the level of the germinating crop and so become phytotoxic. Residual pre-emergence treatment is evidently somewhat hazardous in regions where climatic conditions are unpredictable. Excessive rain can cause gross surface and ground water contamination by herbicides (Flury, 1996). Flury's (1996) review of experimental studies of pesticide leaching showed that pesticide losses below root zone were <0.1% - 1%, reaching up to 4% of applied mass in worst case conditions. If <0.1% of the herbicide reaches the 90 cm depth, the herbicide can contaminate groundwater.

The constant k_{oc}, a measure of the tendency of a compound to partition into soil organic carbon from aqueous solution, is generally inversely related to movement to groundwater (Sanyal and Kulshrestha, 1999). Based on their low k_{oc} values (Table 4) atrazine and metolachlor are expected to maintain a high to medium mobility class in soils. The water solubility values indicate that metolachlor and atrazine are usually associated with the aqueous phase in a two-phase soil-water system and that they leach significantly. In actual fact extensive leaching is reported to occur, especially in soils with low organic matter and coarse texture (EXTOXNET, 1996 and 2000a and US EPA, 2002). Sanyal *et al* (2000) found that applied metolachlor leached down to 15-30cm soil layer. High organic matter, at least two percent, and high clay and/or silt inhibit leaching (EXTOXNET, 2000b). Mobility is thus inversely related to soil organic matter and clay content (Wieterson *et al*, 1993; Obrigawitch *et al*, 1981; Singh *et al*, 2002). Metolachlor readily leached in soil columns, with 34% of the metolachlor found in the leachate (Kim and Feagley, 1998). In soil leaching columns metolachlor was more mobile than atrazine (Seybold and Mersie, 1996; Keller and Weber, 1995). Several studies have been done in temperate zones to assess the leaching potential of pesticides in laboratory and field experiments and to evaluate the influence of soil properties, soil management and application mode on pesticide output from soils. However data on leaching of pesticides in tropical soils are limited in literature (Laabs *et al*, 2002).

As the fate of herbicides in soils is determined by numerous interacting processes (solute transport, degradation, sorption, plant uptake, volatilization and so forth) mathematical models have been developed to understand and to predict pesticide leaching in soils. Leaching models are outlined in section 2.5.3.

2.3.4 Persistence of herbicides

Herbicide persistence, usually compared using half-life ($t_{1/2}=\frac{0.6932}{k}$, where k is the degradation rate constant), is not a fixed property of the herbicide but is influenced by factors such as soil type and weather conditions after application. The primary factors affecting herbicide degradation in soil are adsorption and microbial activity (Ismail and Quirinus, 2000; Hance, 1980; Kearney and Kaufman, 1975). Degradation of atrazine and metolachlor has no lag phase and is more or less proportional to concentration so that results can be interpreted using first–order kinetics (Zimdahl *et al*, 1970; Hance, 1980). Degradation of atrazine and

metolachlor has been reported to obey first-order-kinetics (Zimdahl *et al*, 1970 and Hance, 1980).

$$C = C_o e^{-kt}$$

where C is the concentration after time t, C_o is the initial concentration and k is the rate constant. Since soils are complex biological and chemical media, deviations from simple first-order kinetics have been observed. For example Hance and McKone (1971) showed that first-order kinetics did not precisely describe the breakdown of atrazine in the laboratory, neither did zero order nor half order kinetics. Atrazine and metolachlor are moderately persistent in the soil environment (Deer, 1999), with half-lives of 2.2 to 154 days (Laabs *et al*, 2002; Erickson and Lee, 1989; Akerblom, 1995) and 7.9 to 132 days (Laabs *et al*, 2002; EXTOXNET, 1996 and 2000a; USDA, 1995; and Kollman and Segawa, 2000), respectively. Half lives of atrazine have been reported to decrease with increasing salt concentration and dissolved organic matter (Khan, 1978). The half-lives of herbicides are longer under dry and cold conditions, but significantly reduced where it is hot and humid or when the herbicide is exposed to direct bright sunlight and to high microbial populations (Kearney and Kaufman, 1975). In un amended soils half-lives increase with increasing adsorption and in soils with kaolinite the half lives are shorter than in those with montmorillonite (Buckhard and Guth 1980). Degradation models are outlined in section 2.5.1.

2.4 Degradation of atrazine and metolachlor

Herbicides have been reported to degrade in the environment by microbial, chemical and photo degradation. Degradation of metolachlor and atrazine in soil occurs mainly through microbial decomposition and photo degradation (when sunlight is present). Reactions of atrazine are shown in Figure 8 (Hassall, 1982).

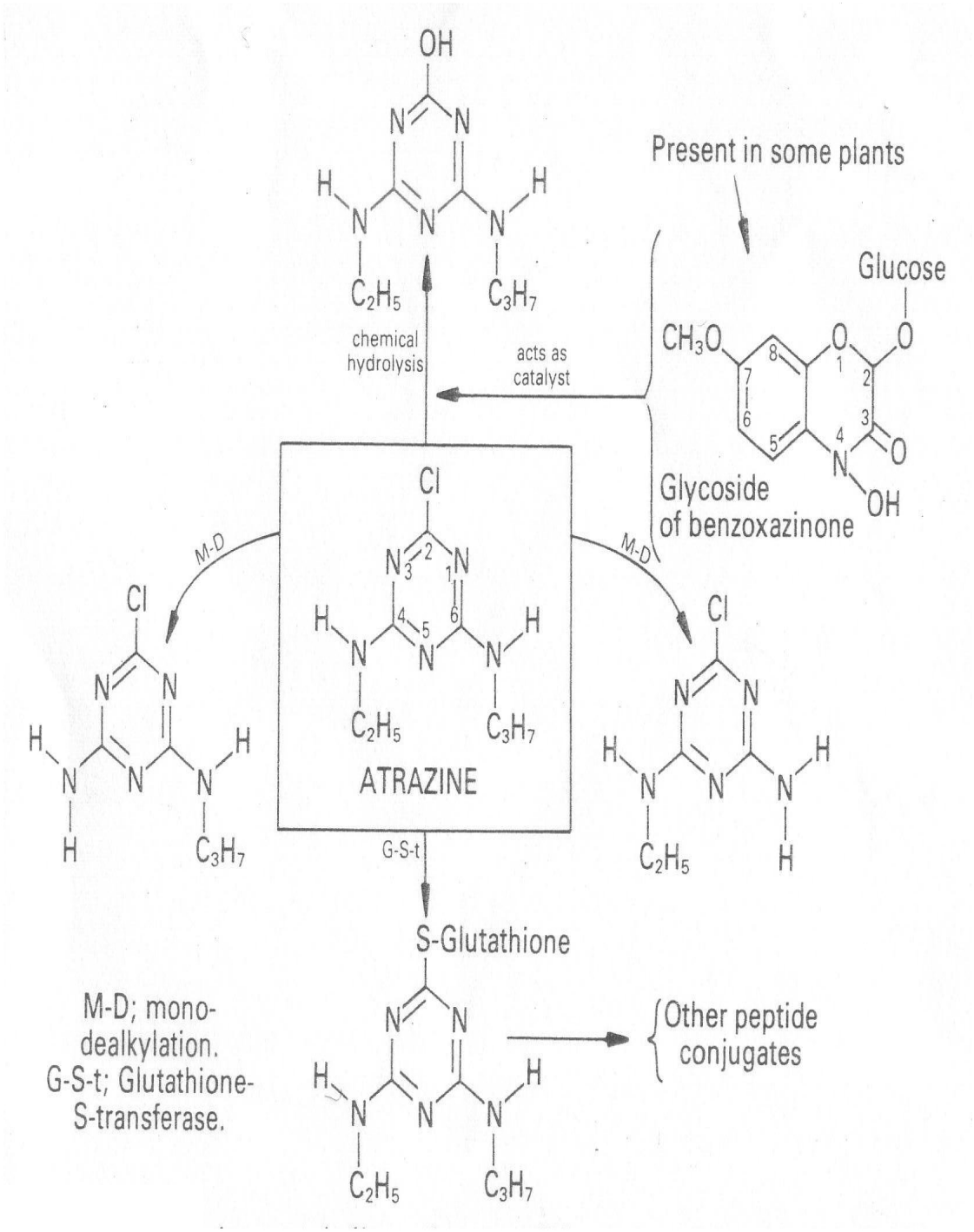


Figure 8: Metabolism of atrazine: three possible routes. M-D, monodealkylation; G-S-t, glutathione-S- transferase; and hydrolysis

Reactions of metolachlor are shown in Figure 9 (Rivard, 2003).

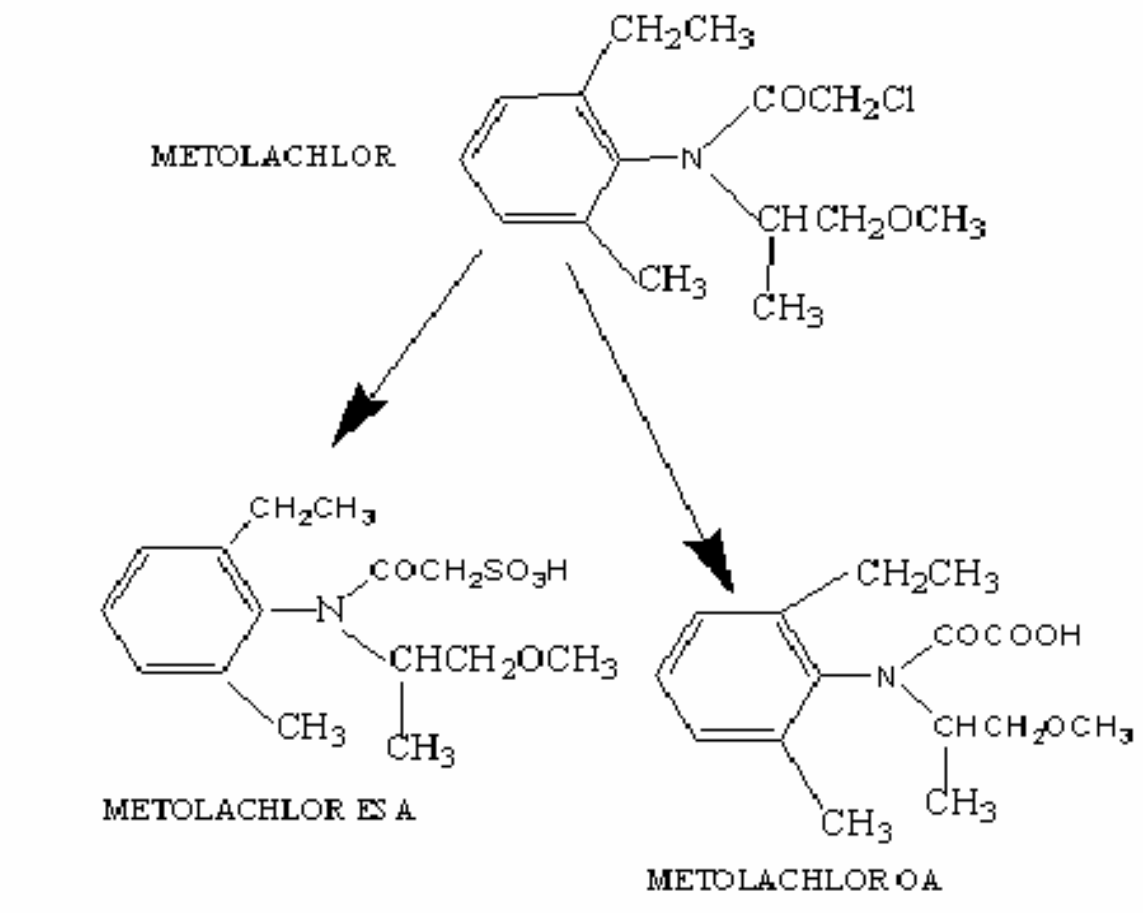


Figure 9: Reactions of metolachlor

2.4.1 Microbial degradation of herbicides

Pesticides are biodegraded when they are mixed with soils. The biodegradation can be aerobic or anaerobic and is affected by temperature, moisture, amount of leaching, soil texture, pH, organic matter, nitrification, aeration, oxygen concentration and sunlight (EXTOXNET, 1996). Pesticide biodegradation has been readily demonstrated by heat sterilization of the soil, by addition of poisons such as mercuric chloride and sodium azide, by appropriate antibiotics or by γ-irradiation, all of which result in complete or very significant reduction in the rate of disappearance of the bioactive material (Cain and Head, 1991). When fresh soil is inoculated into the sterilized samples disappearance of the pesticide is re-established.

Biodegradation of pesticides is viewed as a positive process for reducing environmental hazards. Fungi, bacteria and other micro organisms degrade pesticides by using them as a source of food or energy. Degradation of atrazine and metolachlor is primarily microbial (Shaner and Brien, 2007). Microbial activity accounts for significant degradation of atrazine in soil (US EPA, 2002); especially in soil bound atrazine residues (Barriuso *et al*, 1991). Atrazine can be degraded by *Pseudomonas* sp and *Klebsiella* sp (Cain and Head, 1991).

About 90% of all acetanilide loss is due to microbial degradation (WSSA, 1989). Accinelli *et al* (2001) observed metolachlor degradation only in non-sterile soil. Rice *et al* (2002) observed reduction in the quantity of extractable metolachlor degradates and unextractable soil-bound residues in sterile soil, revealing significance of biodegradation to dissipation of metolachlor in soil.

2.4.1.1 Biodegradation of atrazine

Biodegradation of atrazine occurs via a series of hydrolytic reactions initiated by dechlorination and followed by dealkylation (Park *et al*, 2004). Biodegradation products of atrazine are deethylatrazine, 2-chloro-6-(isopropylamino)-1, 3, 5-triazine-4, 6-diamine, (DEA) and deisopropylatrazine, 2-chloro-4-(ethylamino)-1, 3, 5-triazine-4, 6-diamine, (DIA). DEA is the metabolite of major concern since it is considered as toxic as atrazine while DIA is about 3 to 4 times less toxic (Graymore *et al*, 2001). The water solubilities of DEA and DIA are higher than atrazine's, facilitating the leaching of both compounds (Steinheimer, 1993). Hydroxyatrazine, 2-hydroxy-4-(ethylamino)-6-(isopropylamino)-1, 3, 5-triazine-4, 6-diamine, (HA) can also be formed by biodegradation of atrazine, especially in the presence of high concentration of fulvic acids and at pH <6 (Stevenson, 1994).

2.4.1.2 Biodegradation of metolachlor

Soil micro organisms transform metolachlor to metolachlor ethane sulphonic acid, 2-((2-ethyl-6-methylphenyl) (2-methoxy-1-methylethyl) amino)-2-oxoethanesulfonic acid, (ESA) and oxanilic acid, 2-(2-ethyl-6-methylphenyl) (2-methoxy-1-methylethyl) amino oxoacetic acid, (OA) (Barbash *et al*, 1999). The transformation by soil micro organisms of metolachlor to its degradates, ESA and OA, has been suggested to occur as a result of displacement of the chlorine atom by glutathione, followed by the formation of ESA and OA by different enzymatic pathways (Barbash *et al*, 1999). ESA and OA are more persistent and are found in higher concentrations and more frequently than the parent metolachlor. Kalkhoff and Thurman (1999) reported ESA in 99.7%, OA in 94.3% and metolachlor in 54.1% of the 355

water samples from 12 stream sites in eastern Iowa. Degradates ESA and OA have been found in higher concentrations and more frequently than metolachlor itself in surface water (CDPR, 2002a) and groundwater (CDPR, 2002b) in California. ESA and OA persist in soils for 3 or more years after application (Phillips *et al*, 1999 and Eckhardt *et al*, 1999), and that ESA exceeds OA by a factor ranging from 2 to 5 (Eckhardt *et al*, 1999).

2.4.1.3 Factors affecting biodegradation

Pesticide degradation is affected by soil conditions such as texture, moisture, temperature, aeration, and oxygen concentration, herbicide concentration in soil solution, sunlight, and nitrification, amount of leaching, pH or organic matter (EXTOXNET, 1996; Kontchou and Gschwind, 1998). Addition of pesticide metabolizing microbes to soils, flooding of the soils and addition of dissolved organic matter to the soils have enhanced pesticide degradation (Aislabie *et al*, 1997). Sub soils with less organic matter tend to have less biodegradation than top soils (Walker, 1991). Sanyal *et al* (2000) observed that rate of degradation of metolachlor was faster in soils under flooded partial anaerobic conditions compared to aerobic soil. They also observed that metolachlor was very stable in aerobic soils, with only 49% dissipation in 130 days. Soils with significant soil water content may show more rapid breakdown of pesticides. Atrazine degradation decreases in the presence of high inorganic nitrogen (Rhine *et al*, 2003).

Pesticide biodegradation is also affected by frequency of pesticide application. There is strong positive relationship between the rate of atrazine dissipation in the soil and years of atrazine use on the soil (Shaner and Henry, 2007; Zablotowicz *et al*, 2007). Atrazine dissipation is faster in soils treated with it for a number of years. Repeated applications of the same pesticide have actually stimulated the build-up of micro organisms effective in degrading the chemical (Smith *et al*, 2005). Accelerated biodegradation, once acquired by a soil, can persist for at least two years (Cain and Head, 1991). However, with enhanced herbicide degradation there may be a corresponding loss of weed control efficacy (Zablotowicz *et al*, 2007).

2.4.2 Chemical degradation of herbicides

The resistance of some crops to herbicides, for example the resistance of maize, sorghum, and sugarcane to atrazine, is because the crops contain enzymes that catalyze the detoxification of the herbicides. Some atrazine resistant crops possess one or more glutathione-s-transferases (GSTs) that are used for chemical defence. They catalyze detoxification of xenobiotic

compounds by covalent linking of glutathione (GSH) to hydrophobic substrate, forming less reactive and more polar glutathione s – conjugate (Karam, 1998). Atrazine contains an electrophilic centre, the aryl halogen that accepts an electron pair from the sulphur atom on glutathione to form a covalent bond. Glutathione metabolism is separated into two sequential processes: chemical transformation and compartmentation. These two processes are divided into three phases: phase 1 (activation reactions), phase 11 (conjugation, Figure 10), and phase 111 (internal compartmentation and storage processes). Activation reactions in phase 1 can be hydrolysis, reduction or oxidation. For atrazine this will be cleavage of the reactive chlorine atom in exchange with the S on glutathione (Figure 10).

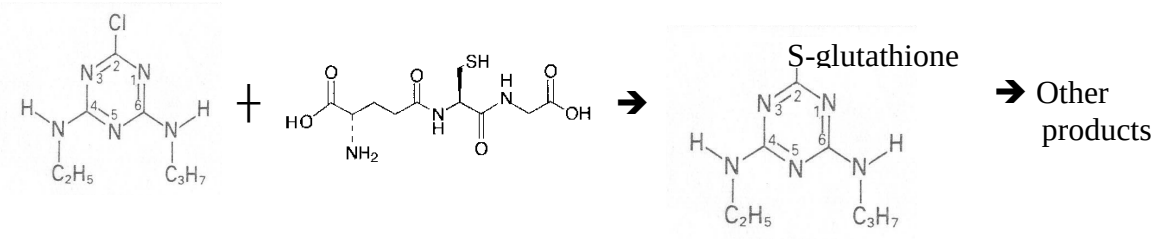


Figure 10: Atrazine and glutathione conjugation reaction

The glutathione conjugation process is enhanced when water has prolonged contact time with the soil and soil enzymes (Phillips *et al*, 1999). All glutathione conjugates are herbicidally inactive (Hassall, 1982). In mammals, rapid and complete metabolism of ingested atrazine is primarily by oxidative dealkylation of the amino group (Hassall, 1982).

Atrazine is metabolized completely mainly by way of oxidative dealkylation of the amino group and reaction of the chlorine atom with endogenic thiolic reagents. Atrazine undergoes non-enzymic but catalyzed hydrolysis, the chlorine atom on C-2 being replaced by a hydroxyl group (Figure 8) (Hassall, 1982; Stevenson, 1994). Atrazine may also undergo N-dealkylation of the secondary amine groups on C-4 and C-6 (Figure 9). The ethyl group is removed from –NHC_2H_5 more rapidly than is the isopropyl group from –NHCH $(CH_3)_2$. Further N-dealkylation, in suitable cases, can lead, eventually, to molecules containing only primary amino groups. Mono dealkylated atrazine is a less effective herbicide than atrazine but it does retain some activity. The partly dealkylated intermediate does not seem to conjugate rapidly with glutathione, so its activity, although limited, often tends to be rather long lasting (Hassall, 1982)

2.4.2.1 Hydrolysis

The most important reaction in chemical degradation of metolachlor and atrazine is hydrolysis. Dissolved organic matter enhances the hydrolysis rates of pesticides (Khan, 1978 and US EPA, 2002). Rate of hydrolysis was found to drastically increase upon small additions of sterilized soil, humic acid and fulvic acid, indicating atrazine hydrolysis is catalyzed (US EPA, 2002). The reaction pathway for hydrolysis of atrazine in the presence of fulvic acid is shown in Figure 11.

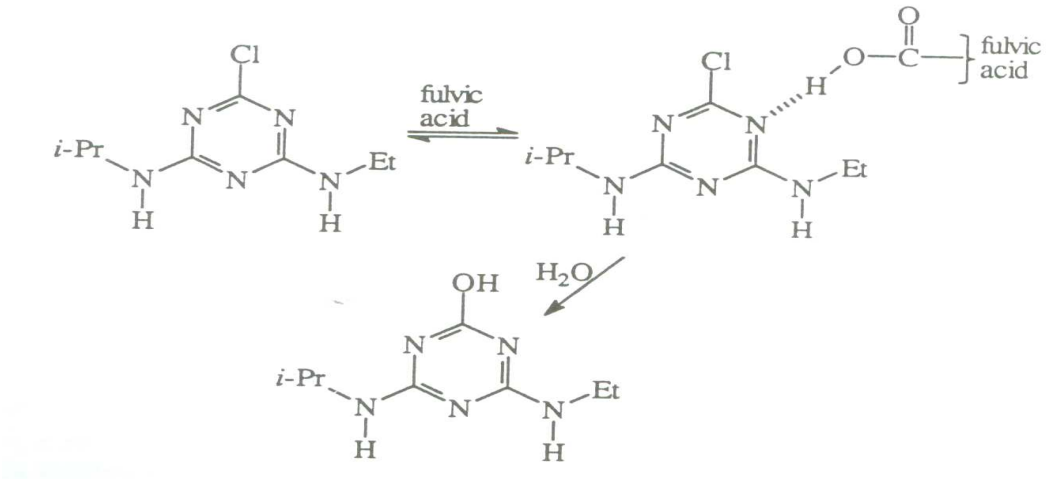


Figure 11: Reaction pathway for the fulvic acid catalyzed hydrolysis of atrazine.

Khan (1978) measured a rate enhancement of a factor of 10 for the hydrolysis of atrazine in the presence of fulvic acid. Choundry (1984) proposed that the observed rate enhancement was due to the interaction of acidic functional groups of the fulvic acid with the ring N-atom adjacent to the C-Cl bond (Figure 11), resulting in the weakening of the C-Cl bond and a lowering of activation energy for hydrolysis.

Hydrolysis is pH dependent. For atrazine, hydrolysis is strongly pH dependent. It mainly takes place under alkaline or acidic conditions. Atrazine is stable in neutral, slightly alkaline or slightly acidic environment (pH 5-11) (Armstrong *et al*, 1967 and US EPA, 2002). Its half-life at pH 5 - 11 can be as high as 10000 days. However, when pH is <3 or pH > 11 hydrolysis is faster, with a half-life of about 90 days (Koch, 1989). In some cases atrazine is completely hydrolyzed within 3-4 days at extreme pH values proceeding twice as rapid in alkaline (pH > 11) than in acidic (pH < 3) media (US EPA, 2002). For metolachlor, hydrolysis is less pH dependent. Metolachlor is highly persistent in water over a wide range

of water acidity. Its half-life at 20^{o}C is more than 200 days for a broad range of pH values (EXTOXNET, 2000a).

Higher temperature and moisture, low pH and high organic matter favour hydrolysis (Armstrong *et al*, 1967). These also favour microbial growth except low pH. Soil pH has greater effect on atrazine degradation than organic matter, with degradation rates decreasing as pH increases (Shaner and Henry, 2007).

2.4.2.2 Photo degradation

Atrazine can be degraded in surface water by photolysis via N-dealkylation and hydroxylation (Figure 12) of the chloro substituent, with corresponding half-lives greater than 100 days at 25^{0}C. These processes also take place in soil, depending mainly on temperature, moisture and pH. Half-lives of 20 – 50 days at 20 – 25^{0}C have been found under laboratory conditions, increasing at lower temperatures (WHO, 2007). However photo degradation of atrazine is of little significance under most field conditions (US EPA, 2002 and EXTOXNET, 1996). Sunlight can be another important degradation pathway of metolachlor in soils.

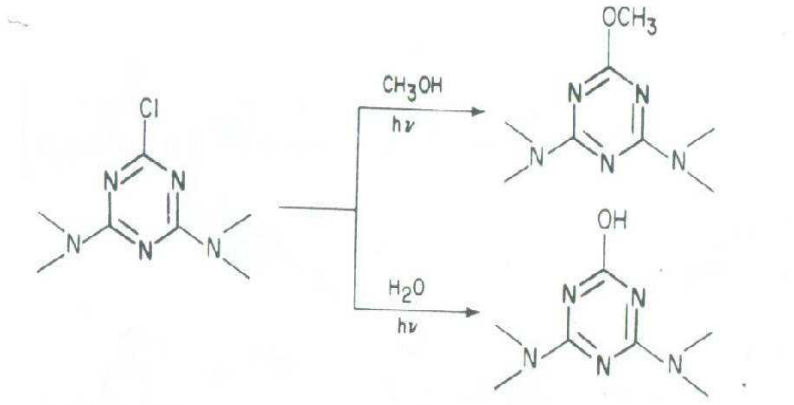


Figure 12: Photo-oxidation reaction of atrazine

It is possible that a majority of the soil-applied metolachlor reaching ground and surface waters through leaching and surface run off is adsorbed on the mineral and organic constituents of the soil, which may influence photolysis in water in different ways. These materials may accelerate photo degradation by energy transfer reactions, photo induced oxidation, or by efficient light scattering. In water hydroxylation, dehalogenation, oxoquinoline formation and demethylation are the main processes of metolachlor photolysis,

the major photolysis product being 4-(2-ethyl-6-methyl phenyl)-5-methyl-3-morpholine (Matthew and Khan, 1996). Metolachlor is relatively stable in water under natural sunlight; about 6.6% was degraded by sunlight in 30 days, a slow and minimal rate (WSSA, 1994). Fifty percent of applied metolachlor on soil surface degrades in 8 days on sunlit soil (WSSA, 1994). However, if the metolachlor is incorporated into the top 2 inches of soil degradation by photolysis is minimal with only 6% degrading over a month (EXTOXNET, 2000a). Photo degradation is a significant degradation pathway only when metolachlor is present in the soil surface.

The photo-oxidation of atrazine affects the chlorine on C-2. When exposed to ULTRA-VIOLET radiation atrazine in aqueous solution degrades to the 2-hydroxy derivative, whereas in alcoholic solution the respective 2-alkoxy derivatives are formed (Figure 12). Under these conditions, 2-methoxy- and 2-hydroxy-1, 3, 5-triazines do not undergo photochemical reactions. In water atrazine absorbs almost no solar ultraviolet-visible and is accordingly quite stable to photolysis, but in presence of large amounts of acetone (about 0.13M), its half-life is decreased considerably (Burkhard and Guth, 1976). At wavelengths greater than or equal to 290 nm, the photolysis half-life of atrazine at a concentration of 10 mg/l in aqueous solution at 15^{o}C was 25 hr as compared to a half-life of 4.9 hr for identical conditions with an acetone sensitizer added at a concentration of 1 ml/100 ml.

2.5 Models

As the fate of pesticides in soils is determined by numerous interacting processes mathematical models have been developed to understand and to predict herbicide behaviour in soils. Most commonly used models are degradation and leaching models.

2.5.1 Degradation models

A large number of kinetic models to describe change in herbicide concentrations with time are available. The FOCUS working group on degradation kinetics has selected several models including simple first order (SFO), a number of models that are able to describe bi–phasic degradation kinetics (bi-exponential or Double - First - Order in Parallel model (DFOP)), Hockey Stick (HS) kinetic model and the biphasic Gustafson and Holden (FOMC) and two models that are suitable to describe degradation patterns with a lag phase (US EPA -EMWG,

2007). The patterns of decline in herbicide concentration with time are illustrated in Figure 13.

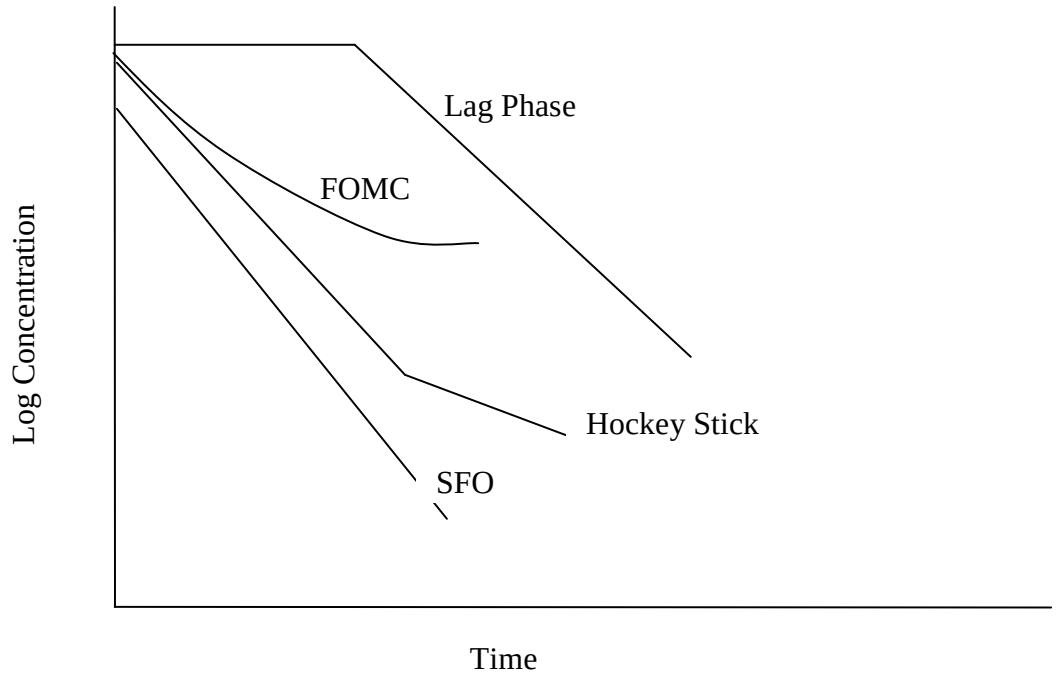


Figure 13: Patterns of decline for herbicide dissipation models

The degradation of atrazine and metolachlor has been reported to have no lag phase (Hance, 1980). Therefore the possible models for degradation of atrazine and metolachlor are SFO, DFOP, HS and FOMC. These are shown in Table 5 (FOCUS, 2006).

The Chi^2 (χ^2) test is used to assess which model provides the best fit to a specific set of data.

$$\chi^2 = \sum \frac{(p-o)^2}{\left(\frac{err}{100}\times \bar{o}\right)^2}$$ where p = predicted value, o = observed value, $\bar{o}$ = mean of all observed values and err = measurement error %.

Calculated chi square value for a specific fit may be compared to tabulated $\chi^2_{m\alpha}$, where m = degrees of freedom which is equal to number of measurements minus number of model parameters and α = probability that one may obtain the given or higher value by chance. Alternatively, the model that best fits the data is the one with lowest χ^2.

Table 5: Chemical dissipation models

Item	Simple First Order (SFO)	Gustafson and Holden (FOMC)	Hockey Stick (HS)	Bi exponential (DFOP)
Equation (integrated form)	$M = M_0 e^{-kt}$	$M = \frac{M_0}{\left(\frac{t}{\beta}+1\right)^{\alpha}}$	$M = M_0\, e^{-k_1 t}$ if $t \le t_b$ $M = M_0\, e^{-k_1 t_b}\, e^{-k_2 (t-t_b)}$ if $t > t_b$	$M = M_1\, e^{-k_1 t} + M_2\, e^{-k_2 t}$ $M = M_0 \left(g\, e^{-k_1 t} + (1-g)\, e^{-k_2 t} \right)$ with $M_o = M_1 = M_2$
Underlying Differential Equation	$\frac{dM}{dt} = -k\, M$	$\frac{dM}{dt} = -\frac{\alpha}{\beta} M \left(\frac{t}{\beta}+1\right)^{-1}$	$\frac{dM}{dt} = -k_1 M$ for $t \le t_b$ $\frac{dM}{dt} = -k_2 M$ for $t > t_b$	$\frac{dM}{dt} = -\frac{k_1\, g\, e^{-k_1 t} + k_2 (1-g) e^{-k_2 t}}{g\, e^{-k_1 t} + (1-g) e^{-k_2 t}} M$
Parameters to be Determined	k, M_0	$M_{0,\ \alpha,\ \beta}$	$M_{0,}$ k1, k2, t_b	M_1, M_2, k_1, k_2 or M_0, g, k_1, k_2

Endpoints				
DT_X	$DT_x = \frac{\ln\frac{100}{100-x}}{k}$	$DT_x = \beta\left[\left(\frac{100}{100-x}\right)^{\left(\frac{1}{\alpha}\right)} - 1\right]$	$DT_x = \frac{\ln\frac{100}{100-x}}{k_1}$ if $DT_x \le t_b$ $DT_x = t_b + \frac{\left[\ln\frac{100}{100-x} - k_1 t_b\right]}{k_2}$ if $DT_x > t_b$	An analytical equation for calculating degradation Endpoints does not exist
Half-life (DT_{50})	$DT_{50} = \frac{\ln 2}{k}$	$DT_{50} = \beta\left(2^{\left(\frac{1}{\alpha}\right)} - 1\right)$	$DT_{50} = \frac{\ln 2}{k_1}$ if $DT_x \le t_b$ otherwise use DT_x above	An analytical equation for calculating degradation Endpoints does not exist

where M(t) denotes the concentration of herbicide still present in soil at time t; k, k_1 and k_2 are dissipation rate constants ($k_1 > k_2$); M_0 is the initial concentration of herbicide in soil; t represents time; t_b is breakpoint time (time at which rate constants change); α is shape parameter determined by coefficients of variation of k values; β is location parameter; g is fraction of M_0 subject to dissipation rate constant k_1 and M_1 and M_2 are the amounts of herbicide subject to the dissipation rates k_1 and k_2, respectively

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Visual assessment can also be used to assess best fits. A graph of predicted versus observed values is plotted and examined for closeness of fit.

2.5.1.1 Simple first-order kinetics (SFO)

Simple first-order kinetics (SFO) is a simple exponential equation with only two parameters. It assumes that the number of pesticide molecules is small relative to the number of degrading micro-organisms and their enzymes or number of water molecules in the case of hydrolysis.

As a result, the rate of the change in pesticide concentration (dM/dt) is at any time directly proportional to the actual concentration remaining in the system. For SFO kinetics, the time for a decrease in the concentration by a certain percentage is constant throughout the experiment and independent of the initial concentration of the pesticide. For example, the time for a decrease in the concentration from 100% to 50% of the initial amount is identical to the time for a decrease from 50% to 25% of the initial amount. This makes DT_{50} and DT_{90} values easy to interpret and SFO kinetics have frequently been used to describe degradation in pesticide fate models. Several reports have indicated departure from simple first order kinetics (Hance and McKone, 1971; Hance, 1980), with reasons given including the following:

- Only the dissolved pesticide is available for degradation. This available herbicide fraction (the herbicide in soil solution) often decreases with time due to slow sorption and diffusion processes (Pignatello, 2000), and this results in a decrease the rate of degradation of the pesticide at later stages of the experiment.
- Non-linear sorption results in a decreasing availability of the herbicide in soil solution with decreasing concentrations, a fast initial decrease in herbicide concentrations will be followed by a slower decline.
- In laboratory degradation studies, the activity of degrading soil micro organisms may decrease with time due to a limited availability of nutrient and carbon sources under laboratory conditions (Anderson, 1987).
- In field studies, seasonal changes in temperature and/or moisture can affect the degradation rate and cause deviations from first-order kinetics (e.g. degradation rate may decrease in cold seasons due to lower temperatures, degradation rate may decrease in summer due to drier conditions).

2.5.1.2 Bi-phasic kinetics

Degradation cannot always be described by SFO kinetics. A fast initial decrease in pesticide concentrations is often followed by a slower decline. This is usually referred to as a bi-phasic pattern of pesticide degradation. The use of a bi-phasic degradation model to fit laboratory data is only justified if the underlying mechanisms are expected to influence degradation under field conditions in a similar manner.

2.5.1.2.1 Gustafson and Holden model

The Gustafson and Holden model considers soil as a spatially variable medium and that the rate of degradation will also be variable throughout the soil. This is accounted for in the model by dividing the soil into a large number of sub-compartments each with a different first order degradation rate constant. The distribution of these rate coefficients is described by a gamma-distribution, which results in a relatively simple analytical equation with only three parameters (Table 5) and gives a bi-phasic overall pattern of pesticide degradation in the soil. This model is also known as First-Order Multi-Compartment model (FOMC). The advantage of the Gustafson and Holden model compared to other bi-phasic models is that it has a relatively small number of parameters. However, the degradation rate is time-dependent. As a result, the Gustafson and Holden model is not appropriate for use in pesticide leaching models.

2.5.1.2.2 Hockey - Stick model

The hockey-stick model consists of two sequential first-order curves. The pesticide concentration initially decreases according to first-order kinetics with a rate constant k_1. At some point in time (referred to as the breakpoint), the rate constant changes to a different value k_2. For typical bi-phasic patterns, the rate constant k_1 is usually larger than k_2. The hockey-stick model has four parameters compared with only three for the Gustafson and Holden model. DT_{50} value for the overall decline of pesticide concentrations is calculated from k_1 if the DT_{50} is reached before the breakpoint. Otherwise the second rate constant, k_2, is used. The hockey-stick model has no advantage over the other bi-phasic models (Gustafson and Holden model and bi-exponential model) with respect to the description of degradation kinetics for parent compounds in soil. It is, therefore, not commonly used. Hockey-stick kinetics is, however, often observed in water-sediment studies (FOCUS, 2006). The hockey-stick model can also be used to derive some input parameters needed in herbicide fate models.

A special case of the hockey-stick model has been recommended as one of the options to describe decline patterns with a lag-phase.

2.5.1.2.3 Bi–exponential model

The integrated form of the bi-exponential model, also known as the Double First-Order in Parallel (DFOP), is a sum of two exponential equations and as a result, the model has no analytical equation for calculation of degradation endpoints. The endpoints must be derived by other means such as reading from herbicide dissipation curves. The half–life for bi-exponential model is **not equal to** $\frac{\ln 2}{k_1}$**.**

2.5.1.3 Lag-phase models

Pesticide concentrations may be virtually constant for a period of time followed by a first-order or bi-phasic decline in pesticide concentration. The initial phase is referred to as lag phase. On some occasions, this can be attributed to storage of soil under conditions that lead to a decrease in active micro organisms prior to the experiment (e.g. excessively air-dried). This is an experimental issue which can be avoided by storing the soil under appropriate conditions. If the lag phase is caused by experimental issues, the lag phase is omitted from kinetic analyses and degradation endpoints are derived from the declining part of the curve only. A true lag phase can be caused by slow adaptation of degrading micro organisms. Degrading micro organisms use some herbicides as a carbon source. The growth of the microbial population and/or the production and release of degrading enzymes is stimulated in the presence of the herbicide. Thus degradation is delayed until the microbial population has reached a certain density or activity. Herbicides showing a lag phase degradation pattern include 2, 4-D, dichlorprop, dalapon and endothal. All data points must be included in the kinetic analysis if a true lag phase exists.

Modified hockey-stick model can be used to describe decline patterns with a lag-phase. Since concentrations remain constant up to the breakpoint, the first rate constant k_1 is set to zero.

2.5.1.4 Logistic model

The logistic model assumes that the degradation rate constant increases after application of the compound up to a maximum value. This could be due to an increase in the number (or activity) of degrading micro-organisms. The kinetics approach first order once the

degradation rate constant has reached its maximum value. The logistic model is used to describe the pattern of decline of the total amount of herbicide residues in soil, M, when a true lag phase with no clear break point exists. Its rate constants are time dependent.

2.5.1.5 Alternative models

A number of alternative models, such as the Michaelis-Menten kinetics, exist. Michaelis-Menten kinetics are useful for describing reactions that are more linear than first order and can be used as an alternative kinetic model where degradation is between zero order (straight line) and first-order. As this type of degradation pattern is not common in environmental fate studies, Michaelis-Menten kinetic models are not usually used. The drawback of this model is that the endpoints depend on the initial concentration of the herbicide (FOCUS, 2006). The Michaelis-Menten kinetics assumes most herbicides are degraded by micro organisms involving enzymes. At the steady state ($\frac{dEM}{dt} = 0$), the rate of enzymatic degradation is described by the following Michaelis-Menten differential equation:

$$\frac{dM}{dt} = \frac{VmM}{Km + M}$$

where EM = enzyme- herbicide (substrate) complex concentration, M = herbicide concentration, Vm = maximum rate of degradation and Km = Michaelis constant. The end point $DT_x = \frac{Km}{Vm}\ln\frac{100}{100-x} + \frac{xMo}{Vm100}$ and $DT_{50} = \frac{Mo}{2Vm} + \frac{Km}{Vm}\ln 2$, where DT_x = time for a decrease in the initial concentration of herbicide of x percent, x = percentage decrease (in concentration) of the initial amount, Mo = total herbicide concentration applied at time t = 0.

2.5.1.6 Choice of degradation models

Models which result in time-dependent or concentration-dependent end-points or which contain a large number of measurements are avoided (FOCUS, 2006). Preference is given to models with a small number of parameters. In a large number of cases, first-order kinetics provides an acceptable fit to degradation data and use of biphasic kinetics is limited to cases where clear deviations from first-order kinetics occur. Current versions of most herbicide fate models [to calculate predicted environmental concentrations of pesticides in groundwater, surface water, soil and sediment within the regulatory framework (PEARL, PELMO, PRZM, MACRO)] are based on first-order degradation kinetics. The implementation of the Gustafson and Holden model, bi-exponential model and hockey-stick model into pesticide fate models is

not universally valid. It should be mentioned that, to date, no degradation model has been identified which meets all criteria (FOCUS, 2006).

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2.5.2 Simple decision aid model for groundwater contamination

Through leaching some of the applied herbicide moves through the soil with water as it percolates down to groundwater. Soil normally filters water as the water moves downward. This filtration leaves the water relatively free of contaminants by the time it reaches groundwater. Soils and herbicides both have properties that influence pesticide movement through the soil to the groundwater. These properties can be combined to rank the ability of each soil type to filter out pesticides, as well as to rank the tendency of each pesticide to leach through the soil.

2.5.2.1 Soil properties and leaching potential

The soil properties that affect pesticide leaching are organic matter, texture and pH. The soil organic matter binds most herbicides very effectively, so the more organic matter in the soil, the less likely an herbicide will leach through the soil. Soil texture (percentage of sand, silt, and clay in a soil) influences how fast water can move through soil. The more sand there is in the soil the easier it is for water and any contaminants to move to groundwater. Soil texture also influences adsorption of herbicides, the higher the clay content the higher the adsorption and the less the leaching. Soil acidity, or pH, affects the chemical properties of many herbicides. Generally as soil pH decreases, herbicides bind more to the clay in the soil and are filtered out of the percolating water. Also, herbicides are usually less soluble in water at lower pH values. Acidity is more important with some types of herbicides than others and is less important overall than organic matter and texture.

Leaching of herbicides is also affected by other geologic and environmental factors such as depth from the soil surface to groundwater. The closer the water is to the surface, the less chance there is for an herbicide to be filtered and degraded in the soil. Weather plays an important role in many ways. Pesticides break down faster in warm, moist soil than in cooler or drier soil. The timing and amount of rainfall or irrigation influence how much water percolates through the soil. If heavy rainfall or irrigation occurs soon after a pesticide application, the percolating water can carry the pesticide deep into the soil where it breaks

down more slowly. Also, the type of tillage practiced can affect soil temperature, moisture, and water infiltration, all of which have an impact on pesticide degradation and leaching.

The three soil properties that affect pesticide leaching—organic matter, texture, and pH—can be combined in an equation to rank soils according to their susceptibility to leaching. The first step in determining soil leaching potential (SLP) is to use the value for each property to place it into a rating category. For example, a soil with an organic matter content of more than 2 percent would have a rating of 10. The rating is then multiplied by an importance factor relative to leaching. The importance factors are 10, 6, and 3 for organic matter, texture, and pH, respectively (McLaughlin *et al*, 1997). These factors are used to emphasize the relative importance of each property. Once the ratings are multiplied by the importance factor for each property, the numbers are added to obtain the SLP (McLaughlin *et al*, 1997).

Soil Leaching Potential (SLP) = Organic Matter (rating x factor) + Texture (rating x factor) + pH (rating x factor)

2.5.2.2 Properties and leaching potential of pesticides

Herbicides have several properties that affect their ability to leach to groundwater, such as k_{oc} *and* persistence ($t_{1/2}$) and their rate of application and placement method. k_{oc} refers to how tightly and quickly the herbicide binds to organic particles in the soil. A higher value indicates a greater tendency for the herbicide to bind to organic matter and a lesser tendency to leach with the soil water. The greater the persistence ($t_{1/2}$) of an herbicide the more likely it is to leach to groundwater.

Different amounts of each herbicide are required to control target weeds. Generally, the chance of leaching increases when pesticides are applied at a higher rate. The application method (F) also affects leaching. Herbicides may be incorporated into the soil by mixing, applied to the soil surface, or applied to growing plants. To leach through the soil, a chemical first has to reach the soil. Pesticides applied to plants can be absorbed by the plant or broken down by sunlight, reducing the potential for leaching. Pesticides applied to the soil surface can also be broken down by sunlight before reaching the soil surface. Of the three methods of application, soil incorporation provides the greatest opportunity for leaching because the entire chemical is placed in the soil. The equation for estimating the leaching potential of an herbicide is (McLaughlin *et al*, 1997):

Herbicide Leaching Potential (HLP) = $\frac{t_{1/2} \times R \times F}{k_{oc}}$ where $t_{1/2}$ is persistence of the herbicide, measured as half-life in days; R is rate of application (pounds of active ingredient per acre); F is fraction of herbicide reaching the soil during application (1 for soil applications, less for post emergent applications, depending on row width and canopy size) and k_{oc} is affinity for soil organic matter. $k_{oc}=\frac{k_d}{f_{oc}}$, where k_d is sorption coefficient and f_{oc} is fraction of organic matter.

2.5.2.3 Groundwater contamination potential

The groundwater contamination potential (GWCP) index was developed to rank the relative risk of applying a specific pesticide to a specific soil. To find the GWCP, the SLP number for the dominant soil series on the field is determined first, followed by the HLP number. Finally, the SLP category for the soil is matched with the HLP categories for the herbicide. Table 6 gives the HLP values with their associated SLP ratings (Murphy, 2006).

Table 6: Groundwater Contamination Potential (GWCP)

Herbicide Leaching Potential (HLP) Rating	Soil Leaching Potential (SLP) Rating		
	<89 Low	90–130 Moderate	>131 High
<1.0 Low	Low Risk	Low Risk	Moderate Risk
1-10 Moderate	Low Risk	Moderate Risk	High Risk
>10 High	Moderate Risk	High Risk	Very High Risk

2.5.3 Leaching models

The models can be used for proper pesticide use. They are particularly useful for structured soils to interpret the complexity of the pesticide transport, and to predict the rapid water flow and pesticide transfer that can occur in such soils, so as to limit the groundwater pollution risk. Different types of mathematical models have been developed in the past (REM, 2000). Some models are more complicated than others with a large number of parameters and with better goodness of fit (Siimes and Kamari, 2003). However these isotherms incur high costs to collect input data. Their goodness of fit is attributed to flexibility gained by the increase in the number of parameters. The real values of the parameters provide information on the properties of the soil and on climate. This goodness, however, decreases as the number of parameters keeps on increasing because the individual parameters can not be estimated independently of each other (Zhu and Selim, 2002). The quality of simulation results depends on the structure of the model and its parameterization. Subjectivity in the derivation of model input parameters is the major source of differences between model results (Boesten, 2000). Boesten (2000) noted that the effect of model user on simulation results was remarkable and that choice of parameters could override model differences in predicting variables.

A model requiring fewer input parameters and less computational efforts is desirable to quickly and accurately predict herbicide fate and transport. The desired model for a particular purpose depends on spatial and temporal scales of the application, and on the available data input. The Register of Ecological Models (REM) database has several pesticide leaching models (REM, 2000). The Forum for the Co–ordination of Pesticide fate models and their use (FOCUS) has recommended models for simulating pesticide leaching (FOCUS, 1996; FOCUS, 2000a). The FOCUS groundwater group (FOCUS, 2000a) selected PELMO, PRZM-2, MACRO and PESTLA to be used in pesticide registration in the EU. Later PESTLA was replaced by PEARL (FOCUS, 2000b). Siimes and Kamari (2003) reviewed all the pesticide leaching models in their simulation of herbicide movement in Finnish sugar beet cultivation. It was reported that none of the models fulfilled all of the desired criteria. However it was noted that MACRO 4.1, GLEAMS 3.0 predicted values were closer to experimental values than other models. Other models they highly regarded were RZWQM, PEARL and PELMO.

General input parameters for PEARL and PELMO models include half-life, soil partition coefficient (k_f), Freundlich exponent (n), soil parameters (% organic carbon, % sand, % clay), biodegradation factor for each soil horizon (DT_{50} or half-life), climate parameters (daily rainfall, daily mean temperature, relative humidity in air and air temperature both at 14.00 hr and potential evapotranspiration) and rate and depth of herbicide application. If volatilization of herbicide is estimated then vapour pressure, water solubility and molecular mass are also required. PELMO considers water flow, surface run off, erosion, subsurface drainage and winter (snow) hydrology. However it does not consider preferential flow (Siimes and Kamari, 2003). PEARL also considers water flow, surface run off, evapotranspiration and subsurface drainage but it does not consider erosion and preferential flow (Siimes and Kamari, 2003). PEARL considers tillage practices but PELMO does not. Atrazine and metolachlor are lost from soils in two ways. Dissolved components are transported with water and adsorbed components are transported with eroded sediment, which in turn is affected by water flow. In PELMO (a capacity model in terms of description of soil moisture and water transport) it is assumed that water flow is driven by water storage rather than water potentials and that downward water flow occurs at maximal rate when field capacity is exceeded. The input parameters required for water flow are soil moisture at field capacity and at wilting point, the total porosity and maximal rate of water flow (which is determined by the saturated hydraulic conductivity of the soil layer. In PEARL (a model which uses Richard's equation to calculate changes in soil moisture content) it is assumed that the direction of water flow is driven by hydraulic potentials and that hydraulic gradient and moisture dependent hydraulic conductivity determine the rate of water flow. The diverse approaches to describing water flow may lead to differences in simulated results for PEARL and PELMO. While PEARL considers tillage practices PELMO does not.

The common outputs from herbicide leaching models are depth and time dependent concentrations of herbicides in the soil profile and concentration of herbicide in the leachate. PELMO is the most commonly used model in pesticide registration (FOCUS, 2000a). It is used to get a first indication of the leaching potential of a pesticide. It has default values for estimation of leaching for screening purposes.

2.6 Analysis of pesticides

2.6.1 Sampling methods

Systematic soil and water sampling methods as well as methods of soil sampling and storage have been reviewed (Cummings, 1966; Beynon and Elgar, 1966). Soil samples are collected using augers. 10-20 cores representing a surface area of at least 200cm^2 are combined, quartered and divided into 1Kg samples for analysis. Surface water samples are usually collected from the middle of the water bodies using weighted sampling bottles. If necessary, samples are taken at various depths and locations across the river. Ground water samples are collected from boreholes and wells. An instantaneous sample (grab sampling) is taken at a given station. A sample container is directly filled with the water to be tested.

2.6.2 Analytical methods

Many of the standard pesticide analytical methods used for environmental samples are the methods approved by federal agencies and organizations such as the US Environmental Protection Agency (EPA) and the National Institute for Occupational Safety and Health (NIOSH). Other methods are those approved by special groups such as the Association of Official Analytical Chemists (AOAC, 2002) and the American Public Health Association (APHA, 1989). Many pesticide analytical methods have been compiled by Zweig and Sherma (1972). The analytical methods include pesticide extraction, clean up and detection. 22 individual publications, four of which refer to simplified methods, on specific procedures are reviewed in the Codex Publication “Recommendations for Methods of Analysis of Pesticide Residues,” CAC/PR 8-1986 (FAO/WHO, 1986b).

Rapid, simple and inexpensive methods have been developed for screening environmental samples for pesticides (US EPA, 1982a). However the methods are potentially inaccurate and are therefore for screening purposes and field applications only.

The classical extraction technique used in the determination of pesticide residues in soil samples has been the solid-liquid partitioning with organic solvents, followed by subsequent cleanup and concentration procedures then detection (using gas or liquid chromatographic determination). The drawbacks of the traditional extraction methods are the use of large amounts of solvents and glassware and the high time consumption. These drawbacks have

been reduced by using other extraction techniques developed recently, which include supercritical fluid extraction (SFE) (Synder *et al*, 1993), solid phase extraction (SPE) with the stationary phase packed in a cartridge or in disks (Redondo *et al*, 1996 and Mogadati *et al*, 1999), and microwave-assisted extraction (MAE) (Lopez-Avilla *et al*, 1995). In addition, a method for the preparation of soil samples based on the sonication of soil samples placed in small columns (SAESC) has recently been developed for the rapid and sensitive analysis of herbicides, insecticides, or fungicides (Perez *et al*, 1998 and Sanchez-Brunete *et al*, 1998). The other drawback is that soil-bound atrazine and metolachlor residues are not detected with standard extraction and analysis procedures (Barriuso *et al*, 1991).

Pesticide analysis should be carried out within the requirements of the CAC Publication "Codex Guidelines on Good Laboratory Practice in Pesticide Residue Analysis," CAC/PR, 7-1984 (FAO/WHO, 1984) and the EU publication 'Quality Control Procedures for Pesticide Residue Analysis', SANCO/3103/2000 (Hill, 1999/2000). Akerblom (1995) has compiled pesticide analytical methods for use in the SADC region.

2.6.2.1 Extraction and clean up of pesticides

Efficient universal extractants for residues of many classes of pesticides in a wide variety of materials include propylene carbonate (Zweig and Sherma, 1972) and ethyl acetate (Sanchez-Brunete *et al*, 2004). Sample material with a low fat and wax content can be extracted directly, separated and analyzed by gas chromatography. Usually, however, it is necessary to clean up the sample; that is to remove the major interfering co-extracted material to avoid deterioration of column performance and to keep the instrument operating properly. Florisil is generally used to cleanup propylene carbonate and ethyl acetate extracts (Zweig and Sherma, 1972; Sanchez-Brunete *et al*, 2004).

2.6.2.2. Detection of pesticides

The great majority of analytical data on pesticides residues have been based on gas chromatography with different detectors, such as nitrogen-phosphorus (NPD) (Perez *et al*, 1998) or electron-capture detectors (ECD) (Synder *et al*, 1994) for organonitrogen and organophosphorus or organohalogen pesticides respectively. The use of GCs with capillary columns provides better separation of components (Sperling *et al*.1985). High-performance

liquid chromatography (HPLC) (Slobodnik *et al*, 1996) has also been employed, particularly when pesticides are thermally unstable.

Gas chromatography coupled with mass spectrometry (GC-MS) is more often used at present for pesticide analysis in soil (Mogadati *et al*, 1999) than the other mentioned detectors due to the possibility of confirming pesticide identity. It should be noted that the use of mass spectrometer as detector is the more definitive method. With this procedure, much of the uncertainty with regard to the identification of the residue is eliminated.

The limit of determination of individual methods depends to a considerable extent on the amount of effort the analyst devotes to extraction and clean-up procedures. With most samples a limit of determination of 0.01mg/kg is normally regarded as acceptable (WHO, 1989)

CHAPTER 3: MATERIALS AND METHODS

3.1 Apparatus

A Pelkin-Elmer LC-75 series liquid chromatograph equipped with a ultra-violet spectrophotometric detector and Supelco ODS hypersil column (5μm, 150mm x 4.6mm) was used to detect atrazine and metolachlor. Sample injection was made using a rotary Rheodyne valve with a 20μl sample loop. A rotary evaporator was used to concentrate clean sample extracts at 40^0C.

A Thermo Electron Corporation centrifuge (IEC Centra CL2) was used to clarify sorption suspensions (separate liquid from solid phases)

Clean glassware was rinsed with acetone followed by hexane or petroleum ether to remove traces of herbicides. Syringes were rinsed with ethyl acetate (Zweig and Sherma, 1972).

3.2 Chemicals and reagents

Analar grade reference standards for atrazine (in solid form) and metolachlor (in liquid form) were obtained from Germany. The main stock standard solution for metolachlor (100mg/l) was prepared by dissolving the 0.1g liquid standard in 1 litre HPLC grade methanol. The 0.1g solid reference standard for atrazine and the stock standard solution for metolachlor were stored in a deep freezer (at -4^0C) pending use. When need arose, the reference standard for atrazine and the stock standard solution for metolachlor were removed from the freezer, allowed to equilibrate to room temperature and used to prepare solutions below and returned to the deep freezer.

Analar grade ethyl acetate, cyclohexane, petroleum ether, dichloromethane, hexane, diethyl ether, calcium chloride, acetone and ammonium chloride and HPLC grade acetonitrile and methanol were obtained from Sigma Aldrich. Commercially available bullet (225g/l atrazine) and dual (960g/l metolachlor) were obtained from Agricultural Trading Company.

3.2.1 Stock atrazine solution in methanol (100 mg/l)

0.10 g of atrazine were dissolved in 250 ml methanol in a beaker, quantitatively transferred to a 1 litre volumetric flask and diluted to the mark with methanol.

3.2.2 Stock atrazine solution in 0.01M $CaCl_2$ (25 mg/l)

25 ml of the 100 mg/l atrazine solution were pipetted into a 100 ml volumetric flask and diluted to the mark with 0.01M $CaCl_2$.

3.2.3 Stock metolachlor solution in 0.01M $CaCl_2$ (25 mg/l)

25 ml of the main stock solution for metolachlor (100 mg/l) were placed (using a pipette) into a 100 ml volumetric flask and diluted to the mark with 0.01M $CaCl_2$.

3.2.4 Atrazine and metolachlor working standard solutions in 0.01M $CaCl_2$ (0.5, 1, 2, 3, 4 and 5 mg/l.

0.5, 1, 2, 3, 4 and 5 mg/l aqueous solutions were made by pipetting appropriate aliquots (0.5, 1, 2, 3, 4, and 5 ml, respectively) of the 25mg/l stock solutions of the individual herbicides to 10ml 0.01M $CaCl_2$ solution in 25ml volumetric flasks and diluting to the mark with 0.01M $CaCl_2$ solution. A stream of nitrogen was passed through the aqueous solutions to remove methanol.

3.2.5 Calcium chloride solution, $CaCl_2$, (0.01M)

2.22g $CaCl_2$ were dissolved in 250 ml de-ionized water, quantitatively transferred to a 2 litre volumetric flask and diluted to the mark with de-ionized water.

3.2.6 Atrazine and metolachlor working standard solutions in methanol (0.5, 1, 2 and 3mg/l

0.5, 1, 2 and 3 mg/l solutions were prepared by pipetting 0.5, 1, 2 and 3 ml of the 100 mg/l atrazine or metolachlor solutions above into 100 ml volumetric flasks and diluting to the mark with methanol. (These were used in obtaining calibration curves for herbicide degradation and mobility studies).

3.2.7 Atrazine and metolachlor spray solutions in de-ionized water (25 mg/l)

250 ml of the 100 mg/l solutions were pipetted into 1 litre volumetric flasks and diluted to the mark with de-ionized water. (Aliquots of these were sprayed on soil surfaces in packed soil columns)

All the stock and working standard solutions above were kept refrigerated (+4^{0}C), until use.

3.2.8 Atrazine and metolachlor spray emulsions (0.18 and 0.384 g/l, respectively)

80 ml and 40 ml of commercially available bullet and dual (for atrazine and metolachlor, respectively) were, separately, dissolved in 100 litres of herbicide free tap water.

3.3 Soil samples

3.3.1 Collection of soils for laboratory sorption, mobility and degradation studies

A range of herbicide-free soil types, with different physical and chemical characteristics, were collected from Ngabu, Thyolo, Bvumbwe, Chancellor College and Makoka in the southern region of Malawi (Figure 14).

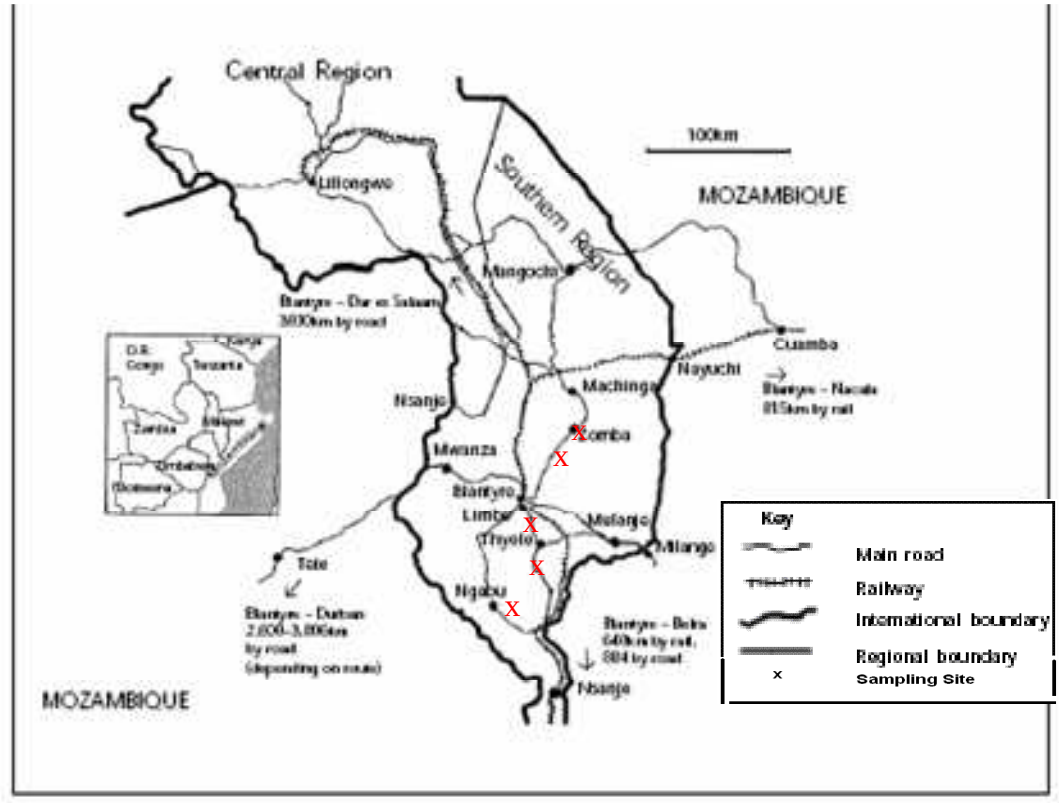


Figure 14: Sampling sites in southern Malawi

The selected sites had no history of application of herbicides and were very far from sites on which herbicides had been applied. The Bvumbwe, Chancellor College, Makoka, Ngabu and Thyolo sampling sites have altitudes of 1146, 885, 1029, 102 and 820 meters above sea level, respectively; latitudes of 15^0 55^1, 15^0 23^1, 15^0 32^1 16^0 30^1 and 16^0 08^1, respectively, and

longitudes of 35^0 04^1 , 35^0 21^1, 35^0 11^1 34^0 57^1 and 35^0 08^1 respectively. Thirty kilograms (30kg) of each herbicide-free soil type were collected, using an auger, from the top soil layer (0 -15cm) at each sampling site. Composite samples of four sub-samples (from four sampling stations per sampling site) were collected. The composite soils were placed in big polyethylene bags, taken to the laboratory where they were air-dried on plastic sheets, sieved through a 6mm sieve and kept in plastic bags at room temperature until use.

3.3.2 Characterization of soils used in field and laboratory studies

Soils were characterized to provide information on soil properties. One kilogram (1kg) samples were taken from each soil type, ground with a porcelain mortar and pestle and sieved through a 2mm sieve. The sieved soils were tested for several chemical and physical characteristics using validated analytical methods adopted by Bvumbwe agricultural research station. The analytical procedures are attached as appendices (Appendix 7.4). Each soil characterization test was duplicated. Aluminium was determined by titrimetric method whereas the other cations were extracted using Mehlich 111 method (Mehlich, 1984) and determined by AAS. Phosphorus, organic matter and nitrogen were determined by the Murphy - Riley's method (Murphy and Riley, 1962), Walkley-Black method (Nelson and Sommers, 1982) and Kjeldahl method (Fox Scientific Inc, 2003), respectively. Percent organic carbon was obtained by multiplying percent organic matter with 0.58 (Morillo *et al*, 2004). Texture (%clay, %sand and %silt) was determined using the hydrometer method and pH was measured in 1:1 soil/de-ionized water mixture. Cation exchange capacity was estimated by adding cations (K + Na + Ca + Mg).

3.4 Selection of extractant for atrazine and metolachlor

Several soil extractants were screened to choose the best extractant under the study conditions. The extractants evaluated were ethyl acetate (Sanchez-Brunete *et al*, 2004), dichloromethane (Akerblom, 1995), acetonitrile (Zweig and Sherma, 1972) and 1:1 v/v acetone/cyclohexane (Akerblom, 1995). For water samples, extractants tested were petroleum ether and ethyl acetate (Akerblom, 1995).

Recovery studies were performed using 2 and 3 mg/l fortification levels for each herbicide. Standard solutions were prepared by diluting the required amount of the herbicide in the required volume of the extractant and stored at 4^oC (Akerblom, 1995).

3.4.1 Herbicide spiking and extraction

3.4.1.1 Soil sample spiking

To each 20g of the five pesticide free soil types, in duplicate, was added 1ml of 2 and 3 mg/l herbicide solutions, separately, before extraction. The spiked soil samples were allowed to stand at room temperature for three hours to achieve complete solvent evaporation and pesticide distribution in the soils (Akerblom, 1995).

3.4.1.2 Soil sample extraction procedure

To 20g of the spiked soil sample in a 250 ml conical flask was added 14ml of 0.2M ammonium chloride, flask was swirled and allowed to stand for 15 minutes and mixed with 100ml of extraction solvent (e.g. 1:1 v/v acetone: cyclohexane). The flask was stoppered tightly, shaken vigorously by hand for 1 minute, shaken less vigorously about every 10 minutes for at least 1 hour and kept overnight. The samples were shaken intermittently for another 2 hours and the contents allowed to settle, after which, de-ionized water was added cautiously until the organic phase filled the neck of the flask. The organic phase was then transferred; using a pipette, into a flask containing 12-15g sodium sulphate (previously dried at 160^0C for 2 hours) and the flask was repeatedly shaken and left to stand for 15 minutes until the drying agent flowed freely. If the drying agent solidified more sodium sulphate was added and swirling repeated until the sodium sulphate flowed freely. The extract was decanted through a plug of glass wool into an evaporation flask (E-flask) {a glass flask with round bottom for evaporating samples on a rotatory evaporator}, sodium sulphate was rinsed with 20-30 ml acetone/cyclohexane and the washings, decanted through the same glass wool plug, were combined with original extract.

3.4.1.3 Water sample extraction with petroleum ether

Two 500 ml aliquots of herbicide free water sample were , each, spiked with 1ml of 3 mg/l herbicide standard solution, transferred into 1 litre separating funnels and mixed with petroleum ether (150ml). The funnels were shaken vigorously for 2 minutes after which the mixtures were allowed to separate for 10 minutes. The aqueous phase was then drained from the funnels into a clean bottle, and the organic phase carefully poured through a 2 cm outside diameter column containing glass wool and 10g of anhydrous sodium sulphate (Na_2SO_4) into an E-flask. The aqueous phases were poured back into the separating funnels for further extraction. The extraction procedure was repeated three times to ensure complete extraction

of the analytes. The organic phase extracts were collected, and mixed, in the same flask. The organic phase was cleaned up as in 3.4.2

3.4.1.4 Water sample extraction with ethyl acetate

Spiked water (1 litre) was saturated with 350g of sodium chloride, divided into two 500ml portions and each portion transferred into a 1 litre separating funnel. The aqueous solution was mixed with sodium chloride (100g), shaken to dissolve, and ethyl acetate (120ml) further added. The funnel was shaken vigorously for 2 minutes, and the phases allowed to separate.

The aqueous phase was drained into clean bottles, while the ethyl acetate phase was poured into a flask containing 15-20g sodium chloride. The water phase was transferred from the bottle into the separating funnels. The bottles were rinsed with 60 ml ethyl acetate and the washings poured into the separating funnel and extracted twice with ethyl acetate (2 × 60ml). The ethyl acetate extracts were collected in the same flask and transferred through a plug of glass wool into an E-flask containing 20g of sodium sulphate. The E-flask was swirled and left to stand for 15 minutes until the drying agent flowed freely. If the drying agent solidified more sodium sulphate was added and swirling repeated until the sodium sulphate flowed freely. The extract was decanted through a plug of glass wool into an evaporation flask, sodium sulphate rinsed with 20-30ml ethyl acetate and the washings decanted through the same glass wool plug, were combined with the original extract. The organic phase was cleaned up as in 3.4.2.

3.4.2. Clean up of extract with florisil

The extract clean up method by Akerblom (1995) was used. A glass column, 10cm long, was packed with 0.5 cm layer of glass wool, florisil adsorbent (30g) and sodium sulphate (5g). The column was washed with petroleum ether (50ml) and washings collected were discarded.

Each sample extract (from 3.4.1.2, 3.4.1.3 and 3.4.1.4 above) was evaporated to dryness on a rotary evaporator at 40^0C. The residue was dissolved in 10ml petroleum ether, transferred into a petroleum ether conditioned column and allowed to penetrate the florisil. The pesticides were eluted with 7% diethyl ether in petroleum ether (200ml) then 25% diethyl ether (200ml).

3.4.3. Pesticide concentration

Each eluate from the clean up column was concentrated by evaporation to about 2ml on a rotary evaporator, and the concentrated solution transferred to a graduated glass test tube placed in a water bath at 38^{o}C, and further evaporated to about 0.4ml for thin layer chromatographic detection.

3.4.4. Pesticide detection

The presence of pesticide was initially confirmed by thin layer chromatography. Samples and standard for atrazine and metolachlor solutions were run on the same chromatographic plate. Atrazine and metolachlor were identified by their retardation factors and quantified by comparing the spots (size and intensity) of sample extracts against those of standard solutions (Akerblom, 1995).

Dipping solution was prepared by dissolving 0.85g silver nitrate in 5 ml de-ionized water, adding 2.5 ml concentrated ammonia solution and diluting to 200 ml with acetone. Ready-made alumina plates were placed into the dipping solution for five seconds then withdrawn and allowed to dry in the fume hood. The dipped plates were stored in a dark place but used within a month.

The development chamber was lined with chromatographic paper. Ethyl acetate (Akerblom, 1995) was poured into the chamber to a level of 1.0 – 1.5 cm to moisten the paper. (This is done to saturate air in the development chamber with ethyl acetate vapour). Equal volumes (0.05ml) of sample extracts and reference standard solutions were applied as bands of equal size onto 20 cm alumina plate, 1.5 cm from the bottom edge, with at least 1 cm left towards the edge of the plate and between bands. The bottom edge of the plate was dipped into acetone in a dish, ensuring that the acetone level did not reach the bands applied. Acetone was allowed to rise to about 1cm above the bands to concentrate them. Then the plate was removed from the dish and acetone allowed to evaporate completely from the plate. The plate was then put in the development chamber and developed, up to 15 cm from the bands after which, it was taken out and the solvent front marked immediately. Then the plate was exposed to ultraviolet light (without filter) from a ULTRA-VIOLET torch at a distance of 11 cm. After two minutes coloured spots were seen and traced. The retardation factors (R_f) were calculated by dividing the distance travelled by herbicide with the distance travelled by

solvent. Concentrations were estimated by comparing intensity and size of sample spots with those of the standards.

3.5 Selection of sampling point for surface water

Water samples were collected from Chipanje river (at Bvumbwe village in Thyolo district), immediately downstream of atrazine and metolachlor treated soils (experimental plots). The experimental plots were irrigated and water samples from the river were taken following the first run off event after herbicide application. The water samples were taken at different distances across the river and at different depths in order to select a suitable sampling point for surface water. The average width of the Chipanje River was 5 meters. For spatial variation in water quality, water samples are collected at 0-5, 5-10, 15-20, 100, 200, 250 (middle), 300, 400, 490-495 and 495-500 cm from the river bank near soils that were treated with metolachlor or atrazine. Water sampling was done on a straight portion of the river and near a bend in the river (C-D and E-F, respectively in Figure 15). For vertical variation in water quality, water samples were taken at various depths 0-5, 15-20, 35-40 and 95-100 cm from the surface. This was for the 100, 250 and 400cm horizontal sampling points.

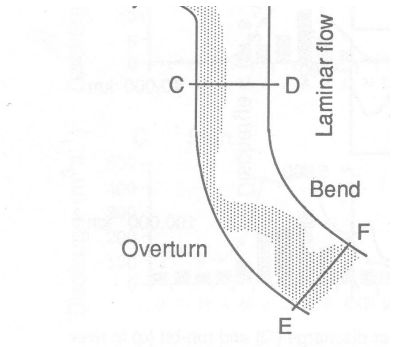


Figure 15: Cross section on a straight portion of river (C to D) and near a bend in the river (E to F)

All glass sampling bottles were thoroughly cleaned and rinsed with de-ionized water as well as ethyl acetate before use to reduce contamination. Each bottle was filled to overflowing and capped, leaving no air space and ensuring that large non homogeneous pieces of detritus, such as leaves, were excluded.

3.5.1 Surface and depth water sampling

To a clean and labelled glass bottle mounted onto a long graduated stick weight was attached. The bottle was lowered into the river, whilst the sampler was standing on the bridge. When the bottle reached the surface of the water, it was positioned in such a way that its mouth faced slightly upwards and towards the current and allowed to fill. The filled bottle was lifted from the water and sealed immediately.

For depth sampling a long clean thin pole was attached to the cover of the bottle (Fig. 16).

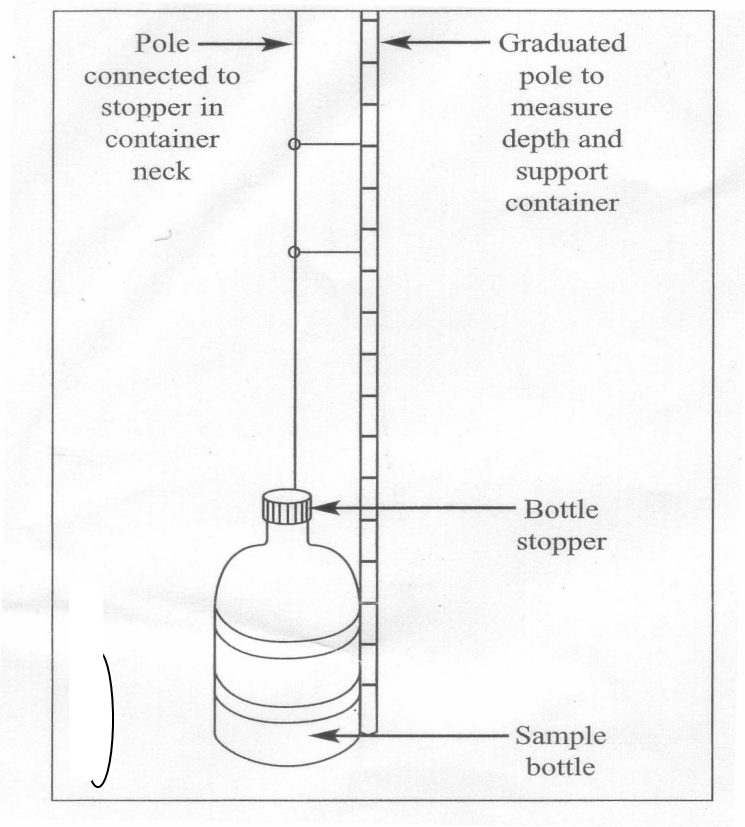


Figure 16: Depth sampling bottle

The bottle was lowered into the river (whilst the sampler was standing on the bridge) until the desired depth mark was reached, cover removed, bottle filled with water, lifted from the water and sealed immediately. Care was taken not to contaminate the water with dirty sticks, weights or bottles.

Water samples from all boreholes, in the study area at Bvumbwe village, were collected using 1 litre glass beakers. Water was pumped for three minutes before collecting water samples. Water sample from the beaker was transferred to a clean glass sampling bottle.

3.5.2 Handling and preservation of water samples

Sealed water sample bottles were stored on ice in a cooler box and quickly transported to the laboratory and refrigerated for analysis within 48 hours of collection (Akerblom, 1995).

3.5.3 Water analysis

The water samples were not filtered before analysis. The unfiltered water sample gives results that best represent what has been transported to the sampling site, including herbicides that are adsorbed on colloidal particles. 1 litre of each water sample was extracted with ethyl acetate as in 3.4.1.4 above. The water sample extracts were cleaned up as in 3.4.2, concentrated as in 3.4.3 and detected as in 3.4.4 above.

3.6 Atrazine and metolachlor residues in water

A snapshot survey was conducted to assess ground and surface water contamination by atrazine and metolachlor in the Zomba/Bvumbwe region. Five ground and sixty-five surface water samples were collected randomly, after the first run-off events, from several rivers in the Zomba/Bvumbwe region during the 2004/2005 rainy season. The ground water samples were collected from wells in farm areas where atrazine and metolachlor were applied. Surface water samples were collected from rivers near farm areas where atrazine and metolachlor were applied. To assess temporal variation in water contamination, water samples were collected systematically at selected sampling points (Table 7) and times (ranging from twice monthly during- to once a month after- herbicide use period). One litre water samples were collected from the surface (0-5 cm deep) within 5 cm from the river bank. The water sample bottles were labelled, placed in a cooler box with ice and transported quickly to the laboratory. The water samples were analyzed within forty eight hours of collection or kept frozen until analysis time. The water samples were analyzed as in 3.5.3 above.

Table 7: Water sampling points for atrazine and metolachlor

Properties of land	Sampling centre				
	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5
Location	Drain, Bvumbwe	Drain, Bvumbwe	Mponda river (behind Chancellor College's maintenance building)	Drain in a tobacco field, Makoka	Chipanje river, Chinkwende village, Bvumbwe.
Near by land use	Smallholder farmer's maize field	Smallholder farmer's tobacco field	Herbicide experimental plot	Tobacco estate	Smallholder farmer's maize field
Topography	Gentle slope	Relatively flat	Gentle slope	Gentle slope	Gentle slope
Herbicides applied	Atrazine 0.9Kg/Ha	Metolachlor 1.44Kg/Ha	Atrazine and Metolachlor	Metolachlor 1.44Kg/Ha	Atrazine 0.90Kg/Ha
Field size	Large	Large	Very small	Very large	Large
Distance between farm and stream	About 100m	About 10m	About 60m	2m	About 60m
Soil texture	Sandy clay loam	Sandy clay loam	Sandy loam	Sandy clay loam	Sandy clay loam
Intensity of rain following herbicide application	Heavy	Light	Light	Moderate	Moderate

3.7 Sorption of atrazine and metolachlor

3.7.1 Adsorption experiment

To 1g (in duplicate) dry soil samples in polypropylene centrifuge tubes was added 5 ml of each working standard solution (OECD, 1981), with concentrations 0.5, 1, 2, 3, 4 and 5 mg/l. Reference samples {herbicide free soil in 0.01M $CaCl_2$ and herbicide standard solutions (with no soil)} were included for background correction and calibration. All tubes (sample and reference) were sealed, shaken end-over-end for 24 hours to ensure equilibration (Abate *et al*, 2004; Krutz *et al*, 2003; Morillo *et al*, 2004; and Oliver *et al*, 2005), and centrifuged for 20 minutes at 1300 revolutions per second after which, 2 ml aliquots of the supernatants were removed (using a pipette, from under the liquid surface of each tube) for herbicide detection. The aliquots (2ml) were then stored in clean cryo vials in a refrigerator until analysis.

3.7.2 Desorption experiment

The soil samples for adsorption studies with initial concentrations (Ci) of 1, 3 and 4 mg/l atrazine or metolachlor were used for desorption studies. The 2 ml removed for LC detection was replaced with 2ml of 0.01M $CaCl_{2,}$ sample continuously shaken for 24 hours, centrifuged and 2 ml aliquots taken as above. For atrazine, desorption process was done for two more 24-hour periods.

3.7.3 Detection of atrazine and metolachlor

Detection of atrazine and metolachlor followed the procedures by Zweig and Sherma (1972) and Akerblom (1995). Cryo vials with samples and 0.5, 1 and 2mg/l working standard solutions were removed from the refrigerator and allowed to equilibrate to room temperature. Atrazine and metolachlor were determined on a liquid chromatograph using the external standardization technique at wavelengths of 210 and 200 nm, respectively, with a mobile phase (HPLC grade methanol) flow rate of 2 ml/min and an injection volume of 100µl (using a micro syringe). Heights of peaks for standard solutions were read from the chromatogram (Appendix 5) and calibration curve was constructed. Heights of peaks for sample solutions were also read from the chromatogram and the concentrations of the samples were read from the calibration curve. Chromatograms for soil samples had many peaks. Atrazine and metolachlor peaks were identified by firstly comparing the soil sample chromatograms with those of their blanks (herbicide free soils) and secondly using the herbicide retention time (distance between sample injection point and herbicide peak on the chromatogram).

The amounts of atrazine and metolachlor adsorbed by the soils were calculated as differences between the amounts in the initial solutions and those remaining in the solutions after centrifugation. The amounts of atrazine and metolachlor desorbed by the soils were calculated as differences between the amounts in the solutions after addition of the 2ml of 0.01M $CaCl_2$ and those remaining in the solutions after centrifugation after desorption shaking.

3.7.4 Data treatment and statistical analysis

Adsorption isotherms were constructed by plotting amount of herbicide adsorbed by soil against the equilibrium solution concentration.

Retention of atrazine and metolachlor in soils was determined by calculating sorption coefficients (k_d) from single-point measurements (batch equilibrium with one concentration). $k_d = \frac{Cs}{Ce}$ where Cs=µmol/kg herbicide adsorbed to soil and Ce=µmo1/l herbicide in equilibrium solution.

Freundlich, Linear, Langmuir and Temkin isotherms were fitted to sorption data for atrazine and metolachlor using equations s_1, s_2, s_3, and s_4 respectively.

Linear	$c_s = k_{dl}\, c_e,$	(s_1)
Freundlich	$\log c_s = \log k_f + n\,(\log c_e)$	(s_2)
Langmuir	$\frac{c_e}{c_s} = \frac{1}{k_1 c_m} + \frac{c_e}{c_m}$ and	(s_3)
Temkin `	$c_s = k_n + k_t \ln c_e$	(s_4)

where c_s = µmol/kg herbicide adsorbed to soil, c_e = µmol/l herbicide in equilibrium solution, c_m = maximum adsorption capacity, k_f = sorption capacity constant µmol/kg and k_{dl}, n, $\frac{1}{c_m}$ and k_t, are slopes of the linear, Freundlich, Langmuir and Temkin plots, respectively; k_n is the adjustable Temkin sorption constant (intercept of Temkin plot), k_1 is the Langmuir sorption constant and n = Freundlich sorption intensity factor. The constant k_f is the amount of herbicide adsorbed for an equilibrium concentration of 1 µmo1/l (Morillo *et al*, 2004). The fitted Freundlich equation was used to determine k_d at a selected Ce (10 µmol/l) in order to calculate the organic carbon normalized distribution coefficient (k_{oc}), using equation s_6.

$$k_{oc} = \frac{k_d \times 100}{\%OC} \qquad (s_6)$$

The k_{oc} is usually used in discussing sorption of non polar hydrophobic compounds.

The hysteresis coefficients, H, for the sorption-desorption isotherms were calculated using equation s_7

$$H = \frac{n_a}{n_d} \qquad (s_7)$$

where n_a and n_d are the Freundlich n constants obtained from the sorption and desorption isotherms, respectively (Morillo *et al*, 2004).

The extent of desorption (D %) was calculated using equation s_8.

$$D\ \% = \frac{A_d}{A_a} \times 100 \qquad (s_8)$$

where A_d is the amount desorbed and A_a is the amount of herbicide initially adsorbed.

Data was analyzed using AGROBASE statistical package for sorption coefficients and GenStat Release 4.24 DE, PC/Windows XP (GenStat, 2005) for k_f and k_{oc}. An analysis of variance (ANOVA) was performed to determine the significance of the effect of soil on the sorption coefficients for each herbicide. The inter-relationships between k_d values and soil parameters (% OC, pH, CEC and % clay) were determined by regression analysis. Means were compared using the least significance difference (LSD) at the 5% level.

3.8 Degradation of atrazine and metolachlor

3.8.1 Herbicide degradation experiment

Each of the five sieved soils (in duplicate) was divided into six 300g portions per herbicide. One portion was sterilized, a second one was acidified (using elemental sulphur) and a third was made more alkaline (using calcium carbonate). The acidified and alkalinized soils were allowed to equilibrate for a day before herbicides were added. In the acidified and alkalinized soils the original pH of the soils was lowered and increased, respectively, by between 1.5 to 2 units. None of the soils had final pH less than 4 or greater than 10. The soil treatments are shown in Table 8. For the flooded treatment, flooding was done immediately after herbicide addition.

Table 8: Soil treatments for herbicide degradation studies

Identity	Treatment of Soil
1	un amended
2	acidified
3	alkalinized
4	anaerobic (sealed)
5	flooded (after herbicide addition)
6	sterilized soil

All the soil portions were moistened to field capacity, 1 ml of 900 and 960 mg/l solutions of atrazine and metolachlor, respectively, added to each of the 300g soil portions, uniformly mixed using a glass spatula and quantitatively transferred to a clean 1litre conical flask and finally sealed with aluminium foil. Treatments 1, 2, 3, 5 and 6 had their aluminium foils perforated to allow air exchange. The samples were kept at room temperature and near glass windows to expose the soils to natural sunlight. Daily room temperatures at 14:00 hours ranged from 22 to 28°C. Moisture contents were maintained at field capacity by addition of appropriate amounts (0 – 5ml) of de-ionized water, based on moisture content determinations.

The experimental design was a completely randomized design (Figure 17) with two replicates.

Figure 17: Soil samples in the degradation experiment

The extent of degradation was assessed by determining atrazine and metolachlor remaining in the soil samples.

3.8.2 Soil analysis

About 35g of each soil sample, in duplicate, were collected for analysis after 0, 7, 14, 28, 56, and 84 days of herbicide application. The collected samples were kept frozen pending

analysis. The frozen soil sample was thawed for 1-2 hours, and thoroughly mixed. Three sub samples were taken, simultaneously, one for moisture determination and two for herbicide determination. The remaining sample was put in a freezer.

3.8.2.1 Moisture content

A known mass of soil sample (about 5g) was put in a pre-weighed Petri dish or beaker, dried at 105^{o}C to constant weight, cooled and reweighed. Then water content was calculated.

3.8.2.2 Herbicide extraction

A known weight of soil sample (about 20g) was put in a 250 ml stoppered conical flask. The soil sample was extracted with ethyl acetate as in 3.4.1.2 above. The extract was cleaned up as in 3.8.2.3 below.

3.8.2.3 Extract clean up

A column consisting of a disposable Pasteur pipette containing glass wool and 1g florisil was washed with hexane (4ml), discarding the washings.

The extract from 3.8.2.2 above was evaporated to dryness. The extract residue was dissolved in 2ml of hexane then quantitatively transferred to the hexane conditioned column. Hexane from the column was discarded. The herbicides were eluted with 2 by 5 ml portions of diethyl ether/ethyl acetate (1:1). The eluate was collected in a clean evaporation flask.

3.8.2.4 Herbicide concentration

Herbicides in the extracts were concentrated by evaporating the extracts to dryness on a rotary evaporator at 40^{0}C. 2ml of methanol were added to the residue in the evaporation flask. After thorough shaking the methanol solution was transferred to a clean cryo vial, which was sealed and stored in a refrigerator, pending detection on a liquid chromatograph.

3.8.2.5 Herbicide detection

Soil sample extracts in cryo vials and working standard solutions for atrazine and metolachlor were removed from the refrigerator and allowed to equilibrate to room temperature. Atrazine and metolachlor were detected as in 3.7.3 above. However the mobile phase, in this case, was HPLC grade acetonitrile/distilled water (30-70%) and the standard solutions were in methanol (instead of 0.01M $CaCl_2$ solution).

3.8.3 Data analysis

The GenStat Release 4.24 DE, PC/Windows XP (GenStat, 2005) was used to generate means and standard errors. The time observed for 50% disappearance (DT_{50}) of atrazine or metolachlor was read from a plot of percent atrazine or metolachlor remaining in soil against time (Loor-Vela *et al*, 2003).

HS, SFO and DFOP models (equations d_1, d_2 and d_3, respectively) were fitted to degradation data using Microsoft excel statistical packages. The fitness of data to SFO and HS models was assessed by coefficients of determination in plots of predicted against observed amounts of herbicides remaining in the soil. Herbicide dissipation was modelled using SFO and HS because, firstly, these models have usually given best fits to degradation data for atrazine and metolachlor (Hance, 1980 and Laabs *et al*, 2002) and, secondly, their dissipation parameters are used in leaching models. DFOP was also used to model dissipation of the herbicides because of its reported better fit quality (FOCUS, 2006).

HS: $C(t) = C_0 e^{-k_1 t}$ if $t \leq t_b$ or $C_0 e^{-k_1 t}\ e^{-k_2 (t-t_b)}$ if $t > t_b$ (d_1)

SFO: $C(t) = C_0 e^{-kt}$ and (d_2)

DFOP: $C(t) = C_1 e^{-k_1 t} + C_2 e^{-k_2 t}$, with $C_0 = C_1 + C_2$ (d_3)

where C (t) denotes the concentration of herbicide still present in soil at time t; k, k_1 and k_2 are dissipation rate constants ($k_1 > k_2$); C_0 is the initial concentration of herbicide in soil, t represents time, t_b is breakpoint time (time at which rate constants change) and C_1 and C_2 are the amounts of herbicide subject to the dissipation rates k_1 and k_2, respectively.

The degradation rate constants for atrazine or metolachlor were estimated by linear regression from the transformed first-order rate equations

HS: $\ln C(t) = \ln C_0 - k_1 t$ if $t \leq t_b$ or $\ln C(t) = \ln C_0 - k_1 t - k_2 (t-t_b)$ if $t > t_b$

SFO: $\ln C(t) = \ln C_0 - kt$,

DFOP: $\ln C(t) = \ln C_1 - k_1 t$ and $\ln C(t) = \ln C_2 - k_2 t$.

The half life for SFO was estimated as $t_{½} = \frac{0.6932}{k}$ (Hance, 1980; Loor-Vela *et al*, 2003).

For HS half-life was equal to $\frac{0.6932}{k_1}$ if the DT50 was reached before the breakpoint time, otherwise the DTx equation in Table 5 was used.

3.9 Mobility of atrazine and metolachlor

Mobility studies included hand packed soil column experiments, with constant water fluxes at fairy high rates, and some experiments under field (rain fall) conditions.

3.9.1 Vertical movement of atrazine and metolachlor in packed soil columns

Homogeneous soil columns were prepared by hand packing, gently and uniformly, moisture corrected soils (Table 9) in 35cm high grade polyvinyl chloride (PVC) pipes of 30 mm diameter which did not adsorb atrazine or metolachlor). The lower end (2.5cm) of each tube was covered with nylon tissue padded with a thin layer of glass wool (0.9g) to hold soil firmly into the column. The top (2.5cm) of the soil in the column was also covered with glass wool to prevent disturbance of the soil by the input deionised water. Soil occupied the length of column, which was graduated at 5 cm intervals, between the top 2.5cm and bottom 2.5cm ends. Care was taken when packing the soil into the column and any subsequent handling and watering to prevent the collapse of soil structure.

All columns were covered with aluminium foil to prevent herbicide evaporation. 2.5 litre glass or polyethylene bottles were placed beneath soil columns to collect leachate (Figure 18).

3.9.1.1 Moisture correction procedure

For moisture treatments 2 and 3 air dried soils were weighed and placed on plastic sheets. Deionised water was added following the percentages shown in Table 9. The soils were thoroughly mixed with the water before transferring them to the columns. For saturated soils (treatments 4 and 5 in Table 9) air dried soils were packed into the columns, soils sub-irrigated until the soil surfaces were wet and subsequently allowed to drain freely for 24 hours.

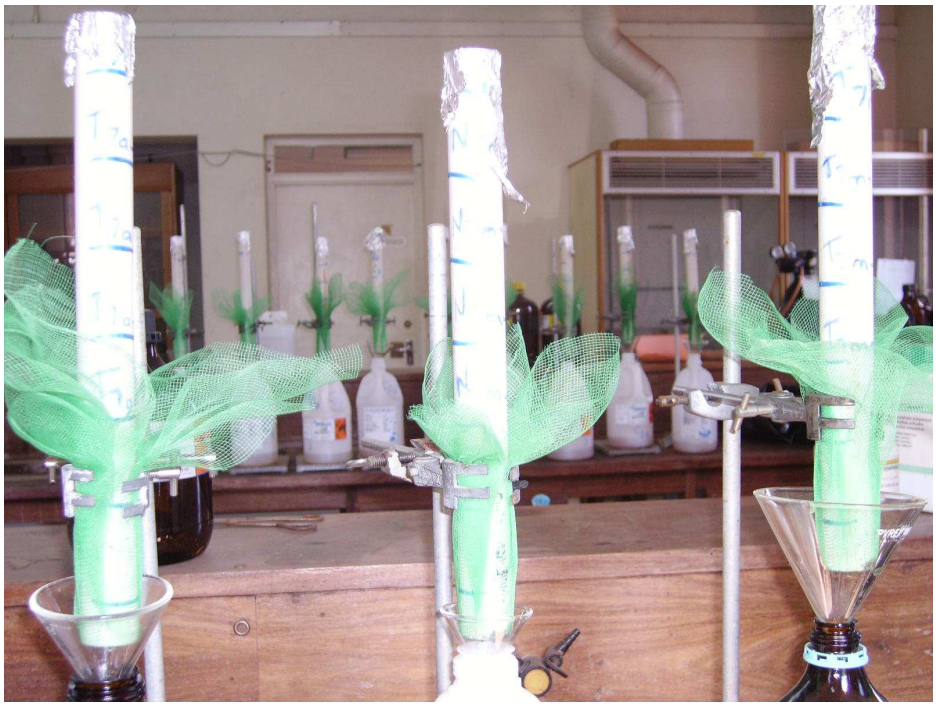


Figure 18: Hand-packed soil columns for leaching experiment

Table 9: Initial moisture content of soils (before addition of herbicides)

Soil Source	Field capacity (%)	Identity of soil sample						
		Moisture content (%)	0	5	7.5	20	100 (saturated)	
		Treatment Number	1	2	3		4	5
		Input water (ml)	520					720
Bvumbwe	3.92		B1	B2	B3		B4	B5
Chanco	12.26		C1	C2	C3		C4	C5
Makoka	10.92		M1	M2	M3		M4	M5
Ngabu	35.14		N1	N2		N3	N4	N5
Thyolo	23.48		T1	T2		T3	T4	T5

Key: B1: B =Bvumbwe (Soil source); (C is Chancellor College, M is Makoka, N is Ngabu and T is Thyolo) and 1 = treatment number 1.

3.9.1.2 Herbicide Leaching

Herbicide emulsions were added evenly on top of the soils using a pipette. 5 ml of atrazine solution (25ppm) were added to Ngabu, Bvumbwe and Makoka soils while 10ml of atrazine were added to Thyolo and Chanco soils. 5 ml of metolachlor solution (25ppm) were added to Ngabu and Bvumbwe soils while 10ml of metolachlor were added to Thyolo, Chanco and Makoka soils. Each packed soil column was labelled XPh where X is site, P is moisture treatment number and h is atrazine or metolachlor. For example B1a was air dry Bvumbwe soil treated with atrazine and B1m was air dry Bvumbwe soil treated with metolachlor.

Several 10ml aliquots of de-ionized water were evenly distributed over the surface of each of the soil columns on each day. The volumes of water added daily ranged from 100 to 150ml, depending on leaching velocity (150ml for Bvumbwe and 100ml for Ngabu soils). At the end of the experiment (8 days), the total volume of water added to treatments 1 to 4 was 520ml and treatment 5 was 720ml. In the N3m soil column application of 520ml of water was not possible due to the low leaching velocities, only 444ml of water were applied.

After 8 days the columns were cut longitudinally and divided into six 5cm sections (0-5, 5-10, 10-15, 15-20, 20-25 and 25-30 cm depth). Each section's soil was thoroughly mixed, bagged and stored in a deep freezer until analysis.

The experimental design was a completely randomized design with two replicates.

3.9.2 Vertical and horizontal movement of atrazine and metolachlor in the field

Herbicide field mobility trials were established at Chancellor College and Bvumbwe village only. Commercially available liquid herbicide formulations, bullet for atrazine (225g/l) and dual for metolachlor (960g/l), were used because most farmers in the country use them. The rates of applications were 1.8 kg/ ha and 3.84 kg/ha or 0.8 ml/m^2 and 0.4 ml/m^2 for bullet and dual, respectively. 1 litre of bullet (0.18 g/l atrazine) or dual (0.384 g/l metolachlor) emulsions were, each, sprayed on 1m^2 experimental plot using a hand sprayer. The herbicide treatments were applied in two blocks. Each treatment within a block was duplicated. The herbicides in the first block were left on the surface whilst those in the second block were incorporated into the soil (soon after application) to a depth of 3cm. (The depth of 3 cm was chosen because weeds which germinate are usually in the top 3 cm of soil although some troublesome weeds

can develop from a depth of up to 12 cm (Hassall, 1982)). No crop was grown on the experimental plots.

3.9.2.1 Soil sampling and analysis

Soil samples (about 250g) were collected at different depths (0-2, 2-5, 5-10, 10-15 and 15-25cm) at several horizontal distances (1, 5, 10, 20, 50 and 100m) from the point of herbicide application and at different times (2, 5, 12 and 30 weeks) from the date of herbicide application using an auger, ruler and small plastic hand shovel. A hole was drilled using the auger. Loose soil was removed from the hole then soil samples collected at different depths by scraping on the sides of the hole were placed in clean and labelled plastic bags which were placed in a big plastic bag and the later were then placed on ice in a cooler box. The samples were transported to the laboratory where they were kept deep frozen until analysis.

Atrazine and metolachlor in the soil samples from packed soil columns and field experiments were analyzed as in 3.8.2 above.

3.9.2.2 Data treatment

A mobility index (MI) was calculated for each herbicide–soil column (Weber *et al*, 2003; Weber *et al*, 2006).

$$\mathrm{MI} = \sum D \times F \qquad (m_1)$$

where D is the mean depth, the distance the herbicide moved (D = 2.5, 7.5, 12.5, 17.5, 22.5 and 27.5 cm) and F is fraction of herbicide present in each soil section (F = herbicide concentration in each soil section divided by total herbicide concentration in soil column sections) (Weber *et al*, 2003; Weber *et al*, 2006).

The maximum value (MI_{max}) was obtained if all the chemical (F = 1.0) was distributed in the bottom (27.5 cm) section ($MI_{\max} = 27.5 \times 1.0 = 27.5$). The smallest ($MI_{min}$) value was obtained if all (F = 1.0) of the herbicide was retained in the uppermost (2.5 cm) section; $MI_{\min} = 2.5 \times 1.0 = 2.5$

The retardation factor, R_f, was also calculated for each herbicide–soil column (Weber *et al*, 2006).

$$R_f = \frac{MI}{MI_{\max}} \qquad (m_2)$$

An analysis of variance (ANOVA) was performed to determine the significance of the effect of soil on the mobility indices for each herbicide. The inter-relationships between MI values and soil parameters (k_d, k_f, % OC, CEC and % clay) were determined by regression analysis. Means were compared using the LSD at the 5% level.

A simple decision aid model was used to evaluate the groundwater contamination potential (GWCP) which was achieved by matching the soil leaching potential (SLP) category of the soil to the herbicide leaching potential (HLP) category (Table 6). SLP was determined by summation of the products of the rating for the soil property and the importance factor of the soil property relative to leaching (10, 6 and 3 for organic matter, texture and pH, respectively).

Soil Leaching Potential (SLP) = Organic Matter (rating x factor) + Texture (rating x factor) + pH (rating x factor) (McLaughlin *et al*, 1997)

Herbicide Leaching Potential (HLP) was calculated using equation m_3.

$$\text{HLP} = \frac{t_{1/2} \times R \times F}{k_d} \quad \text{(McLaughlin } et\ al\text{, 1997)} \qquad (m_3)$$

The k_d was used instead of k_{oc} in equation m_3 because of the exaggerated differences in k_{oc} values of the soils due great differences in organic carbon contents of the soils (Spongberg and Gangliang, 2000).

The PEARL model (FOCUS PEARL, 2006) was used to simulate movement of the two herbicides, to calculate predicted herbicide concentrations in the soil layers at 0.05, 0.1 and 0.2 metre depths at the Bvumbwe site. The PELMO model was not accessible.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Soil characteristics

The characteristics of the soils used for experiments are shown in Table 10.

Table 10: Characteristics of the soils used for sorption, mobility and degradation

Characteristics	Site				
	Bvumbwe village	Chancellor College	Ngabu Bvitula village	Thyolo Kautuka Village	Makoka research Station
Particle Size					
Silt (%)	6	10	22	14	10
Clay (%)	9	19	43	55	23
Sand (%)	85	71	35	31	67
Texture	loamy sand	sandy loam	clay	Clay	sandy clay loam
pH (in water)	5.82	6.24	8.22	6.23	6.52
Organic matter (%)	0.59	1.02	2.84	0.91	0.67
Organic carbon (%)	0.34	0.59	1.65	0.53	0.39
Nitrogen (%)	0.03	0.05	0.14	0.05	0.03
Phosphorus (ppm)	24	14	14	1	22
Potassium (cmol/kg)	1.645	1.459	9.807	5.491	2.798
Sodium (cmol/kg)	0.42	0.46	0.66	0.67	0.51
Calcium (cmol/kg)	4.26	0.96	10.00	0.78	1.29
Magnesium (cmol/kg)	3.31	0.13	0.67	0.24	0.44
CEC (cmol/kg)	8.5	10.94	26.95	18.83	15.53
Water holding capacity:					
Field capacity (0.3 bar)	3.92	12.26	35.14	23.48	10.92
Permanent wilting point (15 bar)	2.42	7.54	23.87	19.08	7.51
Available Water	1.50	4.72	11.27	4.40	3.41
Land use	Agricultural	Agricultural	Agricultural	Agricultural	Agricultural
Dominant clay mineral (Young 1960)	1:1, Kaolinite	1:1, Kaolinite	2:1, montmorillonite and/or vermiculite	1:1, Kaolinite	1:1, Kaolinite

Soil pH ranged from moderately acidic (5.82) for the Bvumbwe soil to moderately alkaline (8.22) for the Ngabu soil. Bvumbwe, Chanco and Makoka soils were low in organic matter and clay contents, with non expanding type clays. Thyolo soil also had low organic matter with non expanding type clays but high clay content. Ngabu soil had high organic matter and clay contents, with expanding type clays. Water holding capacity (WHC) and cation exchange capacity (CEC) were low in Bvumbwe soil, moderate in Chanco, Makoka and Thyolo soils and high in Ngabu soil. Calcium, nitrogen, potassium and sodium were higher in the Ngabu soil than in the other soils. Among the soil properties, organic carbon was correlated to CEC ($r = 0.86$, $p = 0.006$), both were correlated with pH ($r = 0.96$, $p = 0.0001$ and $r = 0.90$, $p = 0.002$, respectively), and CEC was correlated with clay ($r = 0.78$, $p = 0.02$). There was no correlation between clay and organic carbon. The Bvumbwe and Ngabu soils with least and highest, respectively, organic carbon contents and nutrient holding capacities are expected to retain the least and most herbicides, respectively.

4.2 Extractant for herbicides

The precision and accuracy of the procedures obtained by analysis of the herbicides in spiked soil and water samples are shown in Table 11. The individual recovery values ranged from 55 to 85%. Mean recovery values, for fortification level of 4 mg/l, ranged from 68 to 81% with relative standard deviations (RSDs) of 9 and 4%. The recovery values are on the lower end of those reported by other authors (73-98% ± 3-16%, Blasco *et al*, 2003 and 87-106.2% ± 2.4-10.6%, Sanchez – Brunete, 2004). However, all but five are within the range (60-120%) recommended by European Union (Hill, 1999/2000). The recoveries were better for the higher than the lower fortification level. The fortification level of 3 mg/l was, therefore, selected for subsequent analysis.

The results indicated that all extractants gave acceptable recovery values. In soils ethyl acetate and dichloromethane extracted similar amounts of atrazine which were significantly higher than those extracted by acetonitrile or acetone-cyclohexane. For metolachlor, ethyl acetate extracted significantly higher amounts than the other extractants. In water ethyl acetate extracted higher amounts than petroleum ether although the differences were not significant. Ethyl acetate was more preferred because of its generally higher recovery values. It is able to dissolve and extract more compounds in both soils and water (Akerblom, 1995).

Table 11: Recovery of herbicide data (mean recovery, % ± RSD%; n=10)

Soils	Herbicide	Extractant	Fortification Levels	
			3 mg/l	2 mg/l
	Atrazine	ethyl acetate	81 ± 4	78 ± 7
		dichloromethane	79 ± 6	77 ± 5
		Acetone/cyclohexane	69 ± 6	68 ± 8
		Mean ± RSD	76 ± 4	72.5 ± 5
	Metolachlor	ethyl acetate	79 ± 5	76 ± 8
		dichloromethane	75 ± 8	65 ± 10
		acetonitrile	72 ± 6	68 ± 6
		Acetone/cyclohexane	68 ± 9	67 ± 9
		Mean ± RSD	73.5 ± 3.5	69 ± 3.5
Water	Atrazine	ethyl acetate	76 ± 5	
		petroleum ether	71 ± 7	
		Mean ± RSD	72.5 ± 4.5	
	Metolachlor	ethyl acetate	74 ± 6	
		petroleum ether	70 ± 8	
		Mean ± RSD	71 ± 4.8	

Therefore, ethyl acetate was selected as a suitable extractant for atrazine and metolachlor for soil and water samples. Many other authors have used ethyl acetate as a universal extractant for multi (pesticide) residue determination (Sanchez –Brunete, 2004), with good results.

4.3 Sampling point for surface water

The concentrations of metolachlor in the water samples are shown in Table 12. For the straight portion of the river (C-D in Fig. 15), the results indicated that metolachlor was higher near the river bank close to the metolachlor treated soils. The metolachlor concentration was the same for all the sampling points whether vertical or horizontal near the river bend (E-F in Fig.15)

Table 12: Vertical and horizontal distribution of metolachlor concentrations in water of Chipanje river; µg/ml of the cleaned up and concentrated extract (µg/l of water sample).

Depth of water (cm)	Distance from river bank near metolachlor treated soils (cm)									
	0-5	5-10	15-20	100	200	250	300	400	490-495	495-500
	Straight portion of river (C to D)									
0-5	1.5	1.4	1.2	1.0	1.0	1.0	1.0	1.0	1.0	1.0
15-20	-	-	-	1.0	-	1.0	-	1.0	-	-
100	-	-	-	1.0	-	1.0	-	1.0	-	-
	Near a bend in the river (E to F)									
0-5	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
15-20	-	-	-	1.0	-	1.0	-	1.0	-	-
100	-	-	-	1.0	-	1.0	-	1.0	-	-

-: not sampled

In a river with laminar flow, maximum velocities occur in the centre of the river but are reduced to zero at the river bank by frictional forces exerted by the shallow bank zone and the bank itself (Chapman, 1992). This velocity gradient tends to force influent waters to the side of the river where they entered. Concentration therefore, is higher on this side of the river. Such concentration gradients are maintained for less than a kilometre, beyond which perfect mixing occurs (Chapman, 1992). Bends in a river induce mixing leading to uniform concentrations of chemicals across the river.

The effect of sampling depth on metolachlor levels is shown in Table 12. The 0-5 cm depth gave the highest levels such that this was selected for subsequent sampling.

4.4 Herbicide residues in water

4.4.1 Herbicide contamination

The percentage of surface water bodies contaminated by atrazine was higher than that contaminated by metolachlor. Atrazine was detected in thirty eight percent whilst metolachlor was detected in fifteen percent of the water samples. This is in contrast to both the lower application rate of atrazine (0.9kg/ha compared to 1.44kg/ha for metolachlor) and its lower

water solubility (0.033g/l compared to 0.53g/l for metolachlor) but probably consistent with soil and water conservation practices. Atrazine is largely used by smallholder maize farmers whereas metolachlor is mostly used by estate (commercial) tobacco farmers. The latter usually practice better land husbandly management practices than the former hence less export of metolachlor to surface water bodies due to less erosion of the soil. Some estate farmers maintained small percentages of their production areas as chemical (herbicide) filtering land. No atrazine and metolachlor were detected in groundwater from boreholes.

4.4.2 Temporal variation of herbicide concentrations

The effect of time on herbicide levels in surface water is shown in Table 13. The number of pluses indicates relative intensity of the herbicide levels in the water. The results indicate that the relative concentration levels of atrazine were higher than those of metolachlor, probably due to the same soil and water conservation practices mentioned in 4.4.1 above. The highest herbicide concentrations in surface waters occurred following the first run off events and decreased with time; decreasing to zero at 37% of the contaminated sites by the eighth week and at all sites by the twelfth week. The decrease in concentration was probably due to decrease in soil concentrations, which led to lower run off concentrations. [When an herbicide is applied to the soil surface, the initial concentration at the surface immediately begins to diminish due to herbicidal action, microbial and chemical (including photochemical) degradation and volatilization (Guenzi, 1974; Cheng, 1990)].

The results showed that export of herbicides to surface water depends on adsorption and rate of pesticide application. When small quantities of herbicides were applied surface water contamination did not occur, as evidenced by Mponda River (stream 3). Traces of herbicides that may have run off were eventually adsorbed by the soil over which the water ran. Also the clay soil near stream 2 adsorbed herbicide residues, preventing contamination of the stream.

The results showed that surface water contamination depends on upstream and in stream activities. For Chipanje river (stream 5) and stream 1 the upstream water samples had atrazine. This implied that some farmers upstream had applied atrazine on their crop fields. The atrazine may have run off with rainwater from a sprayed land or drifted onto the riverine during herbicide spray elsewhere. According to Hitch *et al* (1995) spray drift can spread up to

Table 13: Occurrence of herbicide residues in surface water samples (Qualitative analysis - TLC method)

Herbicide		Atrazine (++++ for standard)				Metolachlor (++++ for standard)			
Site		A	B	B_1	C	A	B	B_1	C
Stream 1	1	+	+++		++	-	-		-
	2	+	++		++	-	-		-
	3	-	+		+	-	-		-
	4	-	+		-	-	-		-
Stream 2	1			-				-	
	2			-				-	
	3			-				-	
	4			-				-	
Stream 3	1	-	-		-	-	-		-
	2	-	-		-	-	-		-
	3	-	-		-	-	-		-
	4	-	-		-	-	-		-
Stream 4	1		-	-			++	++	
	2		-	-			++	++	
	3		-	-			+	+	
	4		-	-			-	+	
Stream 5	1	++	+++ +		+++	-	-		-
	2	+	+++		++	-	-		-
	3	+	++		++	-	-		-
	4	+	+		+	-	-		-

Key: **1** = sampled within first week of herbicide application, after first run off event; **2** = sampled between second and third weeks of herbicide application; **3** = sampled one month after herbicide application; **4** = sampled two months after herbicide application; **-** means no herbicide was detected and number of pluses indicates relative concentration of herbicide; **A** = upstream of herbicide application area; **B** or **B_1** = within the herbicide application area; **C** = downstream of herbicide application area; **Blank** means herbicide was not determined because either similar point was sampled (B or B_1) or herbicide was not applied close to the that point of the river (stream 2).

hundreds of kilometres. The lower downstream (point C) herbicide levels, for all streams, are possibly due to dilution (mixing of influent with water) and / or in-stream degradation, volatilization or uptake.

The distance between stream and herbicide treated soils also affected herbicide export to surface water. Stream 1 had less atrazine than stream 5 probably because it is further away from the maize field than stream 5. The larger distance meant relatively more chances of adsorption of the atrazine from the run off water by the soils over which the water ran. The extra land, which had grass, acted like a filtering area. According to Sun and Cornish (2003) filtering action is better if land is planted with grass.

The spots for standards for atrazine (2µg/ml) and metolachlor (10µg/ml) gave the highest number of pluses (four pluses). This means that herbicide concentrations in the concentrated water sample extracts were generally less than 2µg/l atrazine or 10µg/l metolachlor. The concentrated extracts were obtained from 1litre of the water sample. Therefore a concentration of 1ug/ml in the concentrated extract means a concentration of 1µg/l (ppb) in the water in the stream. This means herbicide concentrations in the streams were below the WHO allowed limits, 2µg/l atrazine and 10µg/l metolachlor (WHO, 2004). (Only for stream 5, following the first run off events, would the concentration of atrazine have equalled or slightly exceeded the WHO recommended limit).

To prevent export of herbicides to surface water farmers should establish vegetative filter strips. These are narrow strips of permanent vegetation (usually grass) planted adjacent to cropland with the intent to reduce herbicide transport from agricultural application zones. Barfield *et al* (1998) has reported that vegetative filter strips increase the retention time of surface run off and thus reduce herbicide losses through facilitating the deposition of sediment-adsorbed compounds, enhancing herbicide retention by increasing time available for infiltration and sorbing dissolved-phase herbicides to the grass and soil surface.

4.5 Sorption of atrazine and metolachlor

4.5.1 Adsorption of atrazine and metolachlor.

4.5.1.1 Adsorption isotherms

The adsorption isotherms for atrazine and metolachlor are shown in Figures 19a and 19b.

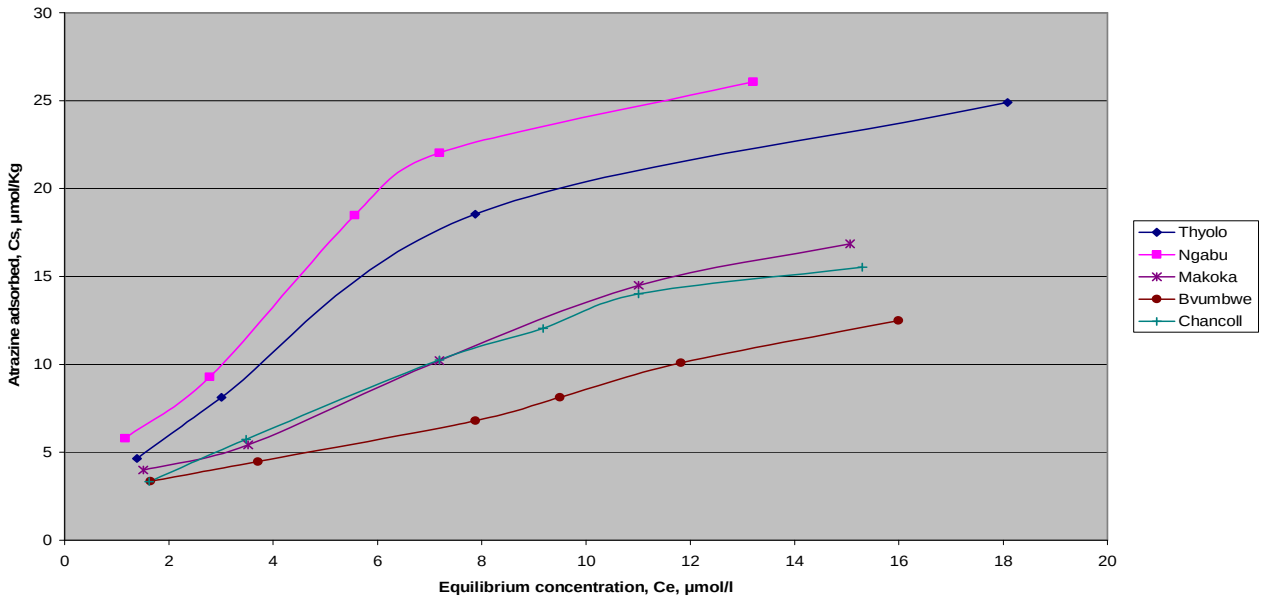


Figure 19a: Adsorption isotherms for atrazine

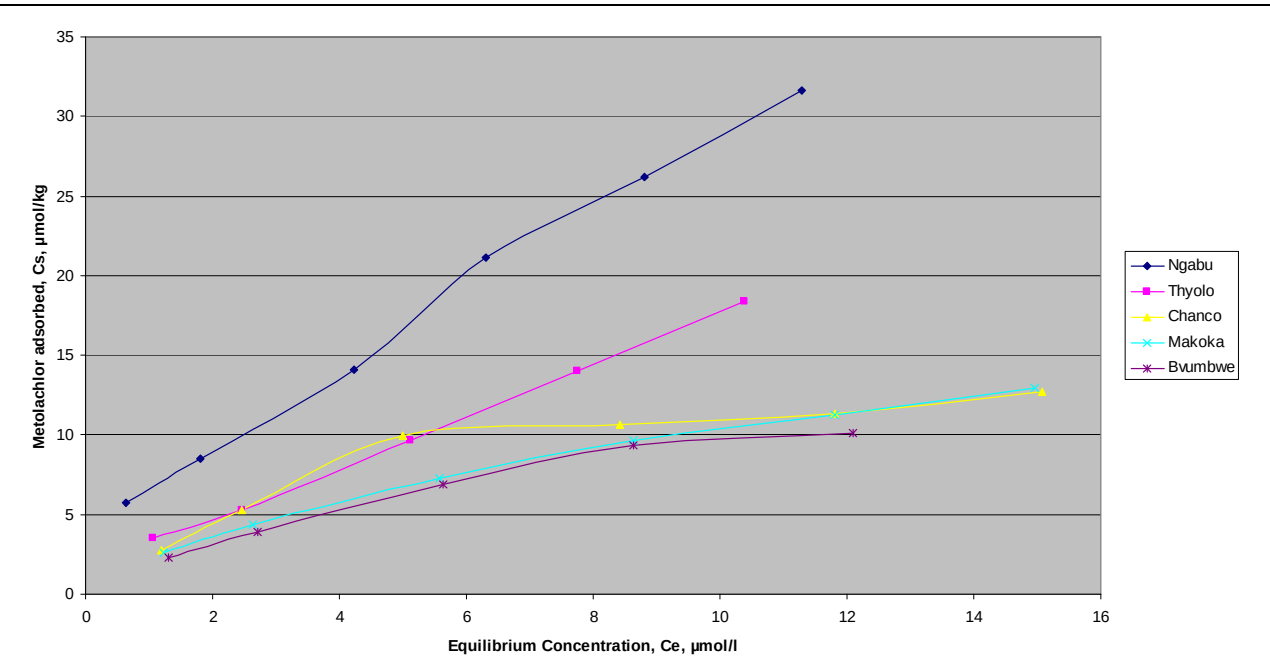


Figure 19b: Adsorption isotherms for metolachlor

The adsorption isotherms were L- type (concave initial curvature) and C-type (linear) (Giles *et al*, 1960). However the linear isotherms were not truly linear, as k_d decreased with increasing initial concentration of herbicide (Table 15). No general rules have been proposed to describe univocally the relation between the shape of isotherms and the nature of adsorbate-adsorbent system (Calvet, 1989).

The adsorption parameters and coefficients of determination (r^2) for the four isotherms are shown in Table 14.

Table 14: Adsorption parameters and fit quality of adsorption isotherms

Herbicide	Soil	Dissipation Parameters							Fit Quality (r^2)			
		Linear	Langmuir		Freundlich		Temkin					
		k_{dl} ml/g	k_l	c_m µmol/kg	n	k_f	k_t	k_n	Langmuir	Freundlich	Temkin	Linear
Atrazine	Bv	0.72	0.21	13.84	0.58	2.29	3.81	0.32	0.88	0.98	0.94	0.99
	Cc	1.03	0.19	19.72	0.72	2.40	5.66	-0.26	0.89	0.99	0.99	0.98
	Ma	1.10	0.18	20.92	0.66	2.76	5.79	0.05	0.86	0.99	0.96	0.99
	Ng	1.97	0.26	32.24	0.67	5.24	8.96	3.00	0.90	0.98	0.98	0.94
	To	1.33	0.19	31.04	0.68	3.88	8.27	0.83	0.91	0.99	0.99	0.95
Mean		1.23	0.21	23.56	0.66	3.31	6.50	0.79	0.89	0.99	0.97	0.97
LSD $_{0.05}$		0.24	0.08	3.743	0.12	1.15	1.58	0.95	0.04	0.04	0.04	0.04
Metolachlor	Bv	0.84	0.26	12.82	0.70	1.96	3.72	0.83	0.89	0.99	0.99	0.97
	Cc	0.78	0.21	14.65	0.58	2.94	3.92	2.26	0.96	0.96	0.98	0.91
	Ma	0.83	0.21	15.17	0.65	2.31	4.14	0.93	0.92	0.99	0.98	0.98
	Ng	2.66	0.34	37.00	0.60	6.77	8.69	6.30	0.87	0.99	0.94	0.99
	To	1.69	0.25	23.05	0.74	3.05	6.30	1.36	0.80	0.99	0.95	0.99
Mean		1.26	0.25	20.33	0.65	3.41	5.35	2.34	0.89	0.98	0.97	0.97
LSD $_{0.05}$		0.83	0.10	3.016	0.15	1.21	1.03	0.50	0.07	0.04	0.05	0.05

Bv=Bvumbwe, Cc=Chancellor College, Ma=Makoka, Ng=Ngabu and To=Thyolo

The atrazine and metolachlor adsorption data fitted well to Freundlich, Linear, Langmuir and Temkin isotherms. However the fits to Freundlich, Linear and Temkin isotherms (r^2 = 0.96 to 0.99, 0.90 to 0.99 and 0.94 to 0.99, respectively) were better than those of Langmuir (r^2 = 0.80 to 0.96). Therefore the adsorption of atrazine and metolachlor was consistent with the isotherms according to the order: Freundlich > Temkin > Linear > Langmuir. Earlier studies

have reported a similar order (Dehghani *et al*, 2005; Singh *et al*, 2001). The Freundlich isotherm gave the best fits and the derived dissipation parameters have been used to discuss sorption of atrazine and metolachlor by the soils. The maximum adsorption capacity is best estimated by the Langmuir isotherm rather than the Freundlich isotherm which has no defined adsorption maximum (Olsen and Watanabe, 1957). The maximum adsorption capacities (c_m) of the soils were Ngabu > Thyolo > Makoka > Chancellor College > Bvumbwe and were significantly different ($p < 0.001$). Therefore, the Ngabu soil has greater adsorption capacity. The observed c_m values are lower than those reported in literature, 692.41g/g for metolachlor (Selim *et al*, 1999) in a very fine smectic Sharkey clay.

4.5.1.2 Adsorption constants

The adsorption constants, k_d, for the two herbicides are presented in Table 15. The k_d values obtained for metolachlor (0.84-9.24) were within the range reported in literature (0.1 – 10; Weber *et al,* 2003). In contrast, the mean k_d values for atrazine (1.10-3.34) were on the lower end of the range reported in literature (2.33-39.6; Abate *et al*, 2004). This was probably due to lower organic carbon content (0.34–1.65%) of soils or due to differences in the types of pools of organic matter in the soils. Oliver *et al* (2005) observed that the pools of organic carbon in tropical soils differed from those of temperate soils. Soil organic matter (humus) binds most pesticides very effectively and is very slowly degradable (McLaughlin *et al*, 1997). Part of the organic matter in the soils under study was not decomposed (such as small pieces of fine roots) so that its ability to bind herbicides was less than that of decomposed organic matter.

The decrease in distribution coefficients, k_d, with increasing initial concentrations of herbicides was probably due to reduced affinity for solute as more adsorption sites became occupied (Abate *et al*, (2004). Adsorption processes arising from heterogeneous site-specific interactions result in decreasing k_d values, leading to n values of less than 1 (Xing *et al*, 1996). It has been reported that adsorption is initially controlled by the solute/surface interactions and later, solute/adsorbed solute interactions become operational (Lengyel and Foldenyi, 2002). Generally, simultaneous adsorption of herbicides to mineral surfaces (clay minerals with their extraneous material coatings such as metal oxides) and partitioning into soil organic matter occurs, followed by diffusion into soil micro pores or into highly cross-linked regions of the soil organic matter.

Table 15: Herbicide sorption coefficient (k_d) values, Freundlich k_f and n values and k_d and k_f ratios for aqueous sorption of atrazine and metolachlor by five soils (Ci = 0.5, 1, 2, 3, 4, 5 µmol/l; 25^{0}C; 24Hr)

	Atrazine (a)				Metolachlor (m)				k_d , k_f ratios	
Soil	Ce (µmol/l)	k_d (ml/g)	k_f (µmo1/kg)	n	Ce (µmol/l)	k_d (ml/g)	k_f (µmo1/kg)	N	$\frac{k_d(m)}{k_d(a)}$	$\frac{k_f(m)}{k_f(a)}$
Thyolo	1.40	3.33			1.1	3.29			0.99	
	3.00	2.69			2.5	2.14			0.80	
					5.1	1.88				
	7.9	2.35								
					7.7	1.8				
					10.4	1.77				
	18.1	1.38								
Mean		2.44				2.18			0.89	
extrp[a]			3.88	0.68			3.05	0.74		0.79
Ngabu	1.2	5.00			0.6	9.24			1.85	
	2.8	3.33			1.8	4.72			1.42	
	5.6	3.32			4.2	3.32			1.00	
	7.2	3.06								
					6.3	3.35				
	13.2	1.98			8.8	2.98			1.51	
					11.3	2.80				
Mean		3.34				4.40			1.32	
extrp[a]			5.24	0.67			6.77	0.60		1.29
Makoka	1.5	2.64			1.2	2.10			0.80	
	3.5	1.54			2.6	1.65			1.06	
	7.2	1.42			5.6	1.30			0.92	
	11.0	1.32			8.6	1.12			0.85	
	15.1	1.12			11.8	0.95			0.85	
					15.0	0.86				
Mean		1.61				1.34			0.87	
extrp[a]			2.76	0.66			2.31	0.65		0.84
Bvumbwe	1.65	2.04			1.3	1.75			0.86	
	3.71	1.21			2.7	1.44			1.19	
	7.88	0.86			5.6	1.22			1.42	
	9.50	0.85								
	11.8	0.85			8.6	1.00			1.28	
	16.0	0.78			12.1	0.84			1.08	
Mean		1.10				1.27			1.16	
extrp[a]			2.29	0.58			1.96	0.70		0.85
Chanco	1.6	2.05			1.2	2.33			1.14	
	3.5	1.65			2.5	2.13			1.29	
	7.2	1.43			5.00	1.98			1.38	
	9.2	1.31								
	11.0	1.27			8.4	1.27			1.00	
	15.3	1.06			11.8	1.02			0.97	
Mean ($\bar{x}$)		1.46				1.75			1.19	
extrp[a]			2.40	0.72			2.94	0.58		1.23
$\bar{x}$, all soils		1.98	3.31			2.23	3.41		1.13	1.02
Significance		***	***			***	***			
$LSD_{0.05}$		0.10	0.10			0.26	0.10			

a Extrapolated to equilibrium concentration of 1.0 µmol/l from the linearized Freundlich equation

Since sorption coefficient characterizes soil/water partitioning it can also be representative for leaching. Weak binding (low k_d) can lead to groundwater pollution where as strong binding (high k_d) can result in surface water pollution through erosion of soil. Soils like the Bvumbwe soil, with lower k_d values are likely to have herbicide leaching problems whilst soils like the Ngabu soil, with higher k_d values are likely to have herbicide run off problems if soil erosion occurs.

The ratios of adsorption coefficients for metolachlor and atrazine ($\frac{k_d(m)}{k_d(a)}$ and $\frac{k_f(m)}{k_f(a)}$) were close to one, indicating that atrazine and metolachlor were adsorbed in similar amounts. Theoretically it was expected that adsorption of atrazine should be higher than that of metolachlor because atrazine has a higher octanol water coefficient, $k_{ow,}$ ($3x10^3$) than metolachlor (794). It has been demonstrated that chemicals with high k_{ow}s are very readily sorbed by natural soil particles in soil/water suspensions (Larson and Weber, 1994). Metolachlor, which is more soluble than atrazine, is expected to associate more with the water phase than atrazine. Factors beyond K_{ow} must be controlling the adsorption, such as the affinity of the adsorption sites for the herbicides, organic matter and clay contents, pH and ionic strength. Hornsby *et al* (1996) found that adsorption of metolachlor was twice that of atrazine, contrally to K_{ow} predictions.

4.5.1.3 Effect of soil characteristics on adsorption

The Freundlich adsorption capacity, k_f, values for atrazine and metolachlor ranged from 2.29 - 5.24μmo1/kg and from 1.96 - 6.77μmo1/kg, respectively. These results are in the broad range of literature data for different soils (0.14 – 4.47 l/kg for atrazine, 0.04 – 5.30 l/kg for metolachlor; Spongberg and Gangliang, 2000) with values for the Ngabu soil being slightly above the higher published values. The adsorption capacities of the soils towards atrazine and metolachlor were significantly different ($p<0.001$). This indicated strong influence of soil characteristics on herbicide adsorption. The difference in adsorption capacity between atrazine and metolachlor in these soils were: atrazine > metolachlor in Bvumbwe, Makoka and Thyolo soils, metolachlor > atrazine in Chanco and Ngabu soils. The n values in the Freundlich equation, which indicate the degree of non linearity between solution concentration and sorption were all less than one for both herbicides and showed a higher non linearity for Bvumbwe soil (atrazine) and Chanco soil (metolachlor).

The complexity of the soils and properties of the herbicides may cause this sorption trend. The data in Table 16 shows that k_d values for atrazine were highly correlated with CEC (r=0.98***), OC (r=0.88**), pH (r=0.88**), nitrogen (r=0.88**) and clay (r=0.81*). The k_d values for metolachlor were highly correlated with OC (r=0.99***), CEC (r=0.89**), nitrogen (r=0.96***) and pH (r=0.94***). Adsorption of both atrazine and metolachlor was not related to soil phosphorus content. The results showed better correlation between adsorption and organic carbon than adsorption and clay. These results are similar to those reported by Spongberg and Gangliang (2000) who concluded that organic carbon is the primary critical parameter and clay content of the soils is the second parameter in herbicide sorption. The role of clay, often masked by that of organic carbon, becomes significant when the clay to organic carbon ratio is greater than 30 (Grundl and Small, 1993; cited in Spongberg and Gangliang, 2000). If this ratio is greater than 62, then 50% of atrazine adsorption is due to clay. In the present study clay/OC ratio varied broadly, 26 for Bvumbwe and Ngabu soils, 32 for Chanco soil, 59 for Makoka soil and 104 for Thyolo soil. In Chanco, Makoka and Thyolo soils, for which adsorption on clay should be significant; atrazine had generally higher k_f values than metolachlor. This may imply that atrazine has generally higher affinity to clay than metolachlor. This was supported by the correlation coefficient values which showed that sorption of metolachlor depended more on organic carbon whilst sorption of atrazine depended more on cation exchange capacity and clay.

Sorption coefficients for atrazine showed weak relationship with clay content while those for metolachlor showed none. For atrazine the relationship between adsorption and clay content may have been affected by differences in the clay mineralogy of the soils. Ngabu soil, with clay/OC ratio of 26, is expected to have insignificant adsorption by clay but this soil has some 2:1 clay minerals (Young, 1964) which have greater adsorption capacity for atrazine than 1:1 clay minerals (Herwig *et al*, 2001). Adsorption is highly dependent on the nature and amount of surface ultimately exposed to the herbicide (Morillo *et al*, 2004). Less clay with 2:1 clay minerals is equivalent to more clay with 1:1 clay minerals. Total surface areas (internal plus external surface areas) and CEC capacities per unit mass of montmorillonite and kaolinite are reported to be 700–800 and 1-15m^2g^{-1}, and 1 and 0.3mol_c kg^{-1}, respectively (Burton *et al* 1994), where mol_c is moles of exchangeable positive charge. The 2:1 clay minerals of Ngabu soil greatly increased the soils adsorption capacity. CEC is a better parameter than mere clay content when soils involved have different clay mineralogies.

Table 16: Correlation coefficients for the relationship between k_d and D (%) with soil characteristics

Soil Parameter	k_d		D (%)	
	Atrazine	Metolachlor	Atrazine	Metolachlor
CEC	0.979 ($p<0.0001$)	0.894 ($p<0.003$)	-0.74	-0.91
Clay	0.814 ($p<0.02$)	0.584 ($p<0.2$)	-0.64	-0.78
Organic Carbon	0.876 ($p<0.004$)	0.986 ($p<0.0001$)	-0.75	-0.85
pH Nitrogen	0.885 ($p<0.005$) 0.88 ($p<0.005$)	0.937 ($p<0.0007$) 0.96 ($p<0.0001$)	-0.73	-0.84

The strong relationship between k_d and OC is consistent with earlier reports by Obrigawitch (1981), Weber *et al* (2003) and Abate *et al* (2004). However, Chanco soil had lower adsorption capacity though with higher organic carbon than Thyolo soil. This may be due to the differences in either clay content or types of pools of organic carbon. Chanco soil adsorbed less herbicide because it had less clay content than Thyolo soil. Several authors have reported that clay minerals play an important role on adsorption of herbicides onto soils (Gilchrist *et al*, 1993; Weber *et al*, 2003; Abate *et al*, 2004; and Weber and Swain, 1993), indicating that organic carbon and clay should be considered together in relation to sorption (Weber *et al*, 1969; Peter and Weber, 1985; and Zhu and Selim, 2000). It is also possible that the soils contained different types of pools of organic carbon. Earlier studies showed stronger relationship between the sorption coefficients and the aromatic and/or alkyl fraction of organic carbon than with total organic carbon (Oliver *et al*, 2005). The Chanco soil may have adsorbed less herbicide because its pool of OC had less affinity for herbicides than the pool of OC in the Thyolo soil. In this study it was not possible to determine aromatic and alkyl fractions of organic carbon.

The dependence of sorption on organic carbon suggests that leaching of atrazine and metolachlor can be prevented by maintaining high organic matter in soils. In this regard organic manure should be added to soils under crops that substantially reduce soil organic matter.

For a particular soil atrazine adsorption decreases with increasing pH (Shaner and Henry, 2007). However the pH values used in the correlation were for different types of soils. The

significant relationship between sorption coefficient and pH could be due to the latter's strong relationship with CEC (r=0.90**) and OC (r=O.96***).

4.5.1.4 Mechanism of bonding

The sorption coefficients normalized with respect to organic carbon content, k_{oc}, values (at equilibrium concentrations of 10µmol/l) are provided in Table 17.

Table 17: Partition coefficients (k_d) and k_{oc} for Ce of 10µmol/l

Source of soil	Partition coefficients			
	$k_{d\ (ml/g)}$		k_{oc}	
	atrazine	metolachlor	atrazine	Metolachlor
Thyolo	1.85 a	1.67 a	349.41a	314.38a
Ngabu	2.44 b	2.72 b	148.05c	164.61c
Makoka	1.28 c	1.03 c	326.96a	263.31b
Bvumbwe	0.87 d	0.97 c	255.56a, b	285.44a, b
Chanco	1.24 c	1.13 c	211.10b,c	191.58c
Mean	1.54	1.50	250	243.90
$LSD_{0.05}$	0.31	0.31	98.60	32.85

Values with different letters down the column are significantly different ($p \leq 0.05$)

The k_{oc} values were generally in the range reported for different soil types (39 – 288 ml/g for atrazine and 22 – 325 ml/g for metolachlor (Spongberg and Gangliang, 2000). However, the k_{oc} values for atrazine in Thyolo and Makoka soils were higher than the published values. This could be due to differences in contribution of clay minerals to the sorption process as these soils had the highest clay/OC ratios in this study. Furthermore, the types of pools of organic matter in these soils could be different from those of the soils in literature reports (Oliver *et al*, 2005). Different pools of organic matter have varying sorption capacities. Many factors (OC, clay, pH and ionic strength) affect adsorption process and therefore result in large differences in calculated, published and actual k_{oc} values (Spongberg and Gangliang, 2000).

The k_{oc} varied from 148.05 to 349.41 for atrazine and 164.61 to 314.38 for metolachlor. Clearly, both hydrophobic and electrostatic interactions were involved in the sorption of the two herbicides to the soils. When hydrophobic bonds are responsible for adsorption of an herbicide on organic matter of soils k_{oc} values are relatively constant among different soils (Morillo *et al*, 2004). The narrower range for metolachlor and the highly significant relationship between adsorption and organic carbon show that hydrophobic bonds play greater role in metolachlor than in atrazine adsorption (Morillo *et al*, 2004).

The significant relationship between sorption coefficients and CEC (Table 16) suggests that the main soil-herbicide interactions are electrostatic (Arias *et al*, 2005). The electrostatic interactions are likely to be Van der Waals forces, hydrogen bonding and formation of coordination complexes. Hydrogen bonding occurs between hydroxides on humus or on the octahedral sheet layers at the surface of clay minerals and the electronegative nitrogen and oxygen atoms of atrazine and metolachlor, respectively. Coordination complexes form when herbicides bond through their electronegative nitrogen or oxygen atoms to the Lewis acid (electron accepting) sites on the humus and clay minerals. Charge (ion–ion) interactions are unlikely because the herbicides in this study are not ionic; metolachlor is non ionisable (Weber *et al*, 2003) while protonation of the atrazine is unlikely at the prevailing soil pH values. The pH is a key factor to controlling the cationic character of atrazine. Atrazine has a pKa of 1.71 (Weber *et al*, 2003). At low pH, the conjugate acid of atrazine reaches significant values, favouring cationic adsorption of the herbicide. Since the pH on clay surfaces is usually lower than the soil suspension pH some protonation of atrazine may have occurred on clay surfaces. Kaolinite, for example, has been shown to have a clay surface pH of about 2 units lower (or a $[H^+]$ of 100 times higher) than the surrounding medium (Larson and Weber, 1994). Thus the Bvumbwe soil (pH 5.82) may have had clay surface pH of about 3.82. Such acidity may have caused limited ionization of atrazine leading to limited ion–ion interactions between negatively charged clay surfaces and the protonated atrazine.

4.5.2 Desorption of atrazine and metolachlor

Desorption of atrazine and metolachlor is shown in Table 18. After the first 24-hour desorption period 0.75 to 40.00 % and 1.33 to 33.91 % of the total atrazine and metolachlor adsorbed, respectively, was desorbed, depending on soils and the initial atrazine and

metolachlor concentrations. In keeping with its higher solubility, metolachlor was desorbed to a greater extent than atrazine (Table 18).

Table 18: Extent of herbicide desorption D (%), with respect to that previously adsorbed during adsorption process

S	24h						48h			72h		
	Ci for atrazine (µg/ml)			Ci for metolachlor (µg/ml)			Ci for atrazine (µg/ml)			Ci for atrazine (µg/ml)		
	1	3	4	1	3	4	1	3	4	1	3	4
To	2.86	4.62	4.66	4.56	11.47	19.10	1.87	2.96	15	dl	2.62	5.41
Ng	0.75	1.17	1.44	1.33	8.47	10.22	0.63	1.02	1.33	dl	1.01	1.13
Ma	12.33	16.8	24.06	12.61	18.23	26.84	3.08	5.60	8.00	dl	4.35	6.72
Bv	10.00	39.00	40.00	16.52	23.64	33.91	15	13.33	14.55	dl	9.43	10.01
Cc	4.04	4.81	4.87	7.06	14.82	22.50	4.56	5.96	7.04	dl	4.58	5.38

To = Thyolo; Ng = Ngabu; Ma = Makoka; Bv = Bvumbwe; Cc = Chancellor College; dl = concentrations for atrazine were below the detection limit; S = source of soil

Table 19 shows cumulative desorption increased with increasing desorption time. However, most of the release occurred in the first 24 hour desorption step. Desorption from soils was hysteretic ($H \neq 1$; Table 19) in all cases, especially for the Ngabu soil, suggesting some irreversible adsorption. Ngabu, with the highest hysteric coefficients had the lowest desorption while Bvumbwe with the least hysteric coefficients had the highest desorption rate.

Table 19: Cumulative desorption of atrazine (D, after 72 hours) and hysteresis coefficients (H, 24 hour desorption period).

Soil	D (%)			H					
	atrazine			atrazine			metolachlor		
	Ci, µg/ml			Ci, µg/ml					
	1	3	4	1	3	4	1	3	4
Thyolo	4.73	10.20	25.07	20	9	7	7	4	1.5
Ngabu	1.38	3.20	3.90	109	89	53	80	40	35
Makoka	15.41	26.75	38.78	17	6	3	2.0	2.0	2.7
Bvumbwe	25.00	61.76	64.56	1.1	1.5	1.9	1.1	0.8	0.9
Chanco	8.60	15.35	17.29	2.5	1.5	1.0	2.5	2.3	1.9

The hysteric coefficients were higher at low adsorbed concentrations (an initial concentration of 1 µg/ml) suggesting that adsorption on soils is more irreversible (lower % D) at low initial (hence adsorbed) concentrations. This suggests that the herbicides were strongly adsorbed at low surface coverage, and therefore it was more difficult for them to desorb. Low herbicide dosages will, therefore, not be effective.

Irreversibility of adsorption plays a significant role in determining the mobility of herbicides in soils. It is inversely related to herbicide run off and leaching that leads to surface and ground water contamination, respectively (Dehghani *et al*, 2005). Irreversibility of adsorption also plays a significant role in determining the availability of herbicide for herbicidal activity (killing weeds). Pronounced adsorption–desorption hysteresis, as in Ngabu soil, is advantageous for use of slow release herbicide formulations. The irreversible adsorption in Ngabu soil means higher amounts of herbicides would be required for the Ngabu soil to maintain adequate herbicidal activity in the soil. Currently recommended rates of application for herbicides are based on crop and soil texture (SNYGENTA, 2004; Chitowe, 2007, *personal communication*). There is need to also consider the clay minerals in the soil as 2:1 clay minerals showed some irreversible adsorption in the Ngabu soil. Farmers can easily identify soils with 2:1 clay minerals from their physical properties. These soils expand when wet and crack when dry.

Desorption was inversely related with organic carbon (r^2 = -0.85 for metolachlor and -0.75 for atrazine), clay (r^2 = -0.78 for metolachlor and -0.64 for atrazine) and CEC (r^2 = -0.91 for metolachlor and -0.74 for atrazine) (Table 16). Ngabu soil with highest organic matter and k_d values showed least desorption for both herbicides. Thyolo soil showed lower desorption percentages than Chanco soil despite having lower organic matter content than Chanco soil, signifying that organic matter and clay should be considered together when assessing desorption.

Greater desorption of metolachlor than atrazine was observed for all but Bvumbwe soils. Desorption of atrazine was limited by its lower solubility in water (30 mg/l compared to 530 mg/l for metolachlor, (US EPA, 2002; EXTOXNET, 1996). In Bvumbwe soil atrazine desorbed more than metolachlor because of weaker interactions between the soil and atrazine. The low H values for Bvumbwe soils indicate the soils least affinity for atrazine, consistent

with the Freundlich's sorption intensity constants (Table 15). Bvumbwe soil had least organic matter and clay but relatively more exchangeable iron and aluminium, indicating relatively more amorphous oxides, which presented an exposed surface with less affinity for atrazine adsorption than the organic surface of the soils.

4.6 Degradation of atrazine and metolachlor

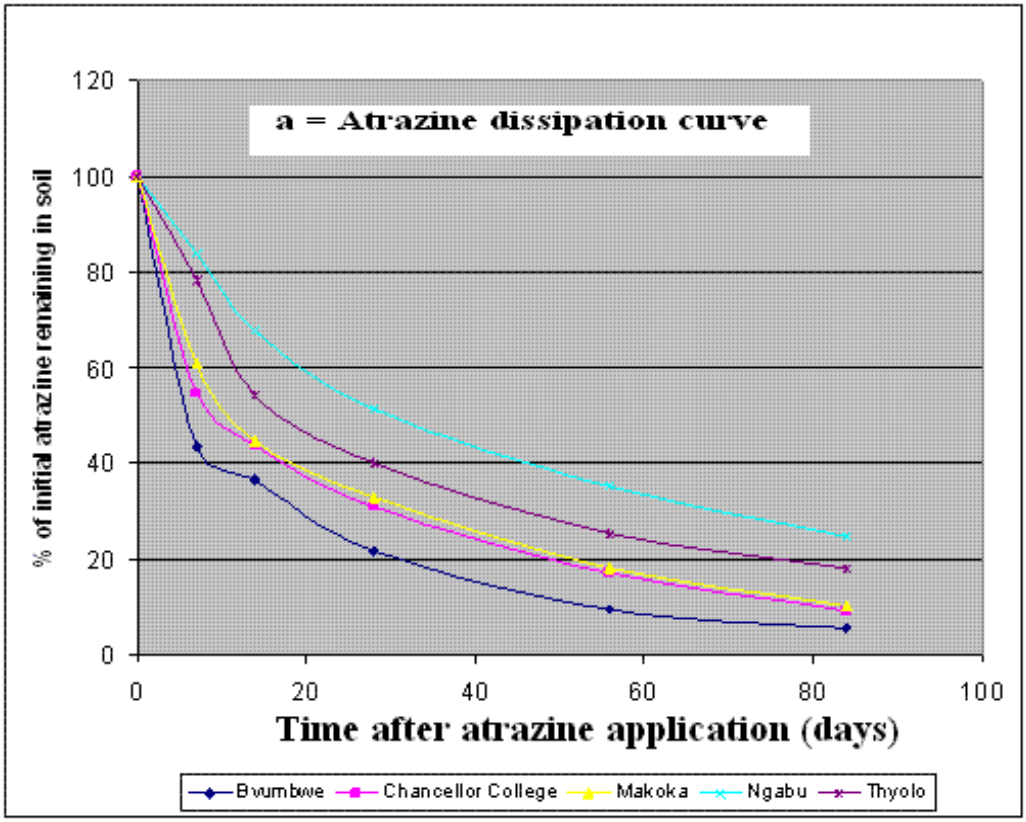
The degradation curves for atrazine and metolachlor are shown in Figure 20.

As expected for most curves of reactions, initial periods of fast herbicide losses were followed by phases of slower degradation. The degradation was disproportionately slow at lower residual concentrations. For soil herbicides, Hamaker and Goring (1976) suggested a 'two component' model to explain this. The herbicide is considered to be divided into available and unavailable portions. Only the available portion (herbicide in soil solution) is subject to degradation. Freshly added herbicide is mainly in the available state and the initial rate of degradation is expected to be rapid. However, the degradation rate falls off as the herbicide transfers to the unavailable state (adsorbed herbicide) and eventually rate of release from the unavailable pool controls the rate of degradation.

4.6.1 Fit quality of simple first order (SFO), bi-exponential (DFOP) and hockey stick (HS) kinetic models

The raw data in Figure 20 (also in appendix 7.1) were fitted to various models. The degradation constants and quality of fit for SFO, DFOP and HS models for the unamended soils are shown in Table 20. The three models SFO, DFOP and HS models provided nice fits for atrazine (r^2 = 0.97 - 0.99, 0.99 and 0.91 – 0.98, respectively). The first order degradation processes of atrazine in all soils were consistent with earlier studies (Accinelli *et al*, 2001; and Seybold *et al*, 2001). However, some authors have reported atrazine degradation which did not follow zero, half or first order kinetics (Hance and McKone, 1971).

The three models SFO, DFOP and HS models also provided nice fits for metolachlor (r^2 = 0.97 - 0.98, 0.97 - 0.98 and 0.91 – 0.99, respectively). The first order degradation processes of metolachlor in all soils are consistent with earlier studies (Ismail and Quirinus, 2000), although Seybold *et al* (2001) had reported zero order degradation kinetics for this herbicide.



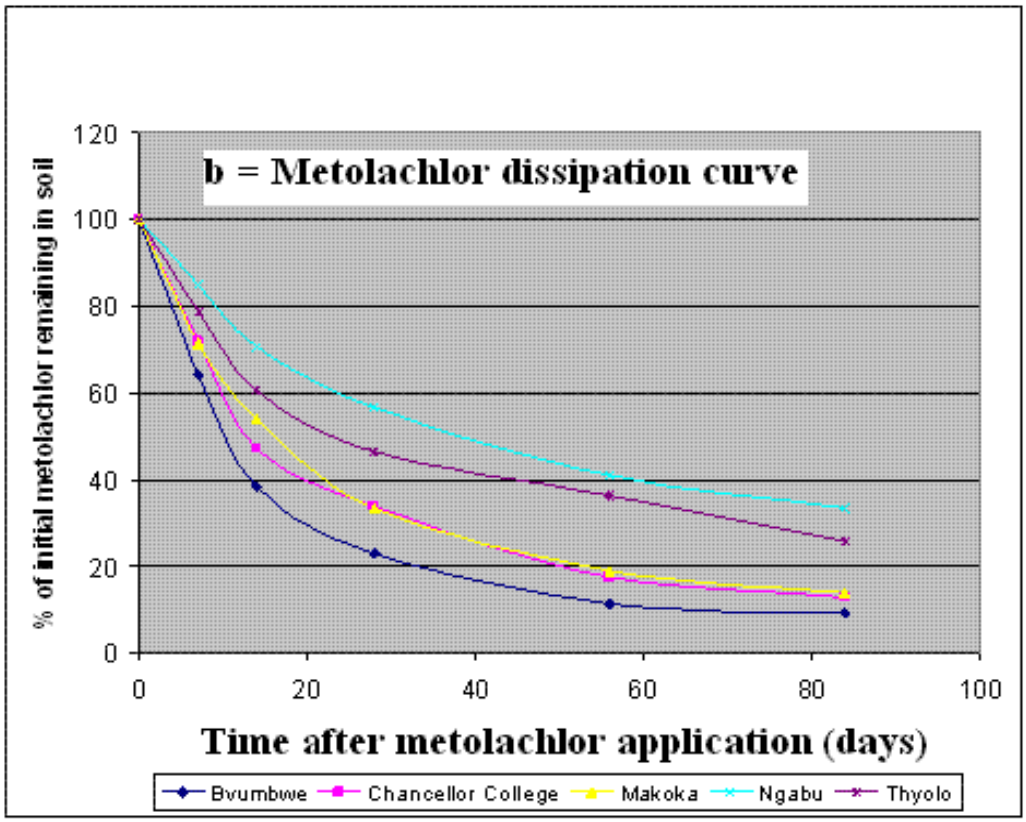


Figure 20: Dissipation curves for atrazine (a) and metolachlor (b)

Table 20: Dissipation parameters and fit quality data for SFO and HS models

Herbicide	Soil	DT_{50} (days)	Dissipation parameters									Quality of fit (r^2)		
			SFO			Bi exponential Models						SFO	DFOP	HS
Atrazine			C_0 µg/g	k mean rate (day^{-1})	$t_{1/2}$ (days)	C_0 µg/g	C_1 % of C_0	k_1 mean rate (day^{-1})	C_2 % of C_0	k_2 mean rate (day^{-1})	HS $t_{1/2}$ (days)			
	Bv	6	0.053	0.0314	22	0.053	78.30	0.1294	21.70	0.0152	5.4	0.97	0.99	0.98
	Cc	10	0.064	0.0258	27	0.064	69.22	0.1420	30.78	0.0250	4.9	0.98	0.99	0.96
	Ma	12	0.055	0.0250	28	0.055	67.27	0.1220	32.73	0.0220	5.7	0.98	0.99	0.92
	Ng	30	0.037	0.0163	43	0.037	48.65	0.0640	51.35	0.0180		0.99	0.99	0.91
	To	20	0.0276	0.0196	35	0.0276	59.78	0.0580	40.22	0.0110	11.9	0.97	0.99	0.93
Mean		15.60	0.0473	0.0226	31.30	0.0473	64.64	0.1021	35.36	0.0182	6.97	0.979	0.99	0.94
$LSD_{0.05}$		7.96	0.0078	0.0084	4.945	0.0138	6.905	0.0076	6.315	0.0061	2.159	0.0467	0.028	0.084
Metolachlor	Bv	10	0.5329	0.0279	25	0.5329	77.14	0.1409	22.86	0.0132	4.9	0.95	0.99	0.92
	Cc	13	0.740	0.0238	29	0.740	66.22	0.1703	33.78	0.0277	4.1	0.97	0.97	0.91
	Ma	16	0.241	0.0233	30	0.241	66.60	0.0489	33.40	0.0085	14.2	0.97	0.98	0.94
	Ng	35	0.120	0.0128	54	0.120	43.33	0.0183	56.67	0.0055		0.98	0.98	0.99
	To	24	0.280	0.0149	46	0.280	53.57	0.0522	46.43	0.0104	13.3	0.97	0.97	0.95
Mean		19.6	0.383	0.0205	36.8	0.383	61.4	0.0861	38.63	0.0131	9.14	0.969	0.969	0.942
$LSD_{0.05}$		11.95	0.0085	0.0019	9.34	0.0489	9.50	0.0023	7.36	0.0013	4.448	0.0665	0.073	0.120
Bv=Bvumbwe, Cc=Chancellor College, Ma=Makoka, Ng=Ngabu and To=Thyolo														

On the basis of r^2 values, the atrazine and metolachlor dissipation conformity to the models can be arranged in the following order: DFOP > SFO > HS. Considering the bi-phasic nature of the dissipation curves in Figure 21, the bi-phasic HS model was expected to give better fit than SFO. The poor fit of HS model was probably due to use of an extrapolated t_b value rather than from calculation.

The SFO half –lives (Table 20) varied from 22 – 43 days for atrazine and 25 – 54 days for metolachlor at 25^0C. These values fell within the ranges reported for atrazine (2.2 to 154 days, Laabs *et al*, 2002; Erickson and Lee, 1989; and Akerblom, 1995) and metolachlor (7.9 – 132 days, Laabs *et al*, 2002; EXTOXNET, 1996 and 2000a; USDA, 1995; and Kollman and Segawa, 2000). It is interesting that the half-lives based on HS model were more similar to DT_{50} values but not those based on SFO which use an average rate constant for the whole degradation period rather than the rate constants for the fast and slow degradation periods used in HS model (FOCUS, 2006)**.** The rate of degradation (in the unamended soils) was generally slower for metolachlor than for atrazine. This was consistent with earlier results (Laabs *et al*, 2002). However, others have reported shorter half-lives for metolachlor than for atrazine (WSSA, 1994). Significant differences ($p< 0.01$, $p<0.002$) were observed among the soils. The herbicides generally persisted much longer in soils with higher k_d, thus soils with higher organic carbon and clay contents.

The persistence of herbicides in soils was highly correlated with herbicide adsorption to soil particles (r =0.99 for atrazine and r = 0.92 for metolachlor), organic carbon (r = 0.83 for atrazine and r-0.77 for metolachlor), cation exchange capacity (r= 0.97 for atrazine and r=0.93 for metolachlor) and clay (r =0.88 for atrazine and r=0.92 for metolachlor) and nitrogen content of the soils (r=0.84 for atrazine and r=0.80 for metolachlor) (Table 21). Peter and Weber (1985) and Buckhard and Guth (1980) also reported that half lives increased with increased adsorption. Shaner and Brien (2007) found that nitrogen deficiency (low soil N) promoted biodegradation of N-heterocyclic compounds, such as atrazine and to some extent metolachlor, in soil. Rhine *et al* (2003) also established that atrazine degradation increased in the presence of low inorganic nitrogen in soil. The microbial community in soil needs nitrogen for their growth. If the soil has inadequate nitrogen, microbes get their nitrogen,

through biodegradation, from organic nitrogen containing compounds, such as atrazine, which are added to the soil. Triazines are nitrogen sources for bacteria (Cook and Hutter, 1981)

Table 21: Correlation coefficients for the relationship between half life (SFO) and soil characteristics

Soil parameter	Atrazine	metolachlor
CEC	0.97	0.93
Clay	0.88	0.92
Organic Carbon	0.83	0.77
Nitrogen	0.84	0.80
k_d	0.99	0.92

Half lives affect both leaching and herbicidal activity. Leaching is directly related to herbicide longevity. The Ngabu soil with higher longevity should retain herbicides for longer periods of time. This will enhance leaching by increasing time available for infiltration. Higher longevity also means prolonged herbicidal action. However if an herbicide is very persistent it may harm following crops, making the land unusable for many growing seasons (Hassall, 1982).

These results indicate that, for Ngabu soils, the residual herbicidal phytotoxic effects would impact on the next crop. For the Bvumbwe soil with low herbicide persistence split herbicide application may be more effective than one (dumped together as one) herbicide application.

4.6.2 Effect of saturation, sterilization, acidification, alkalinization and inadequate oxygen on herbicide degradation

The effect of soil treatment on degradation of atrazine and metolachlor is shown in Tables 22 and 23, respectively.

Table 22: Effect of soil treatment on degradation of atrazine

Soil	Soil treatment	Total loss (%)	Atrazine (µg/g) Sampling time, days					
			0	7	14	28	56	84
Bvumbwe	1 (unamended)	94.3	.053	.023	.019	.011	.005	.003
	2 (acidified)	94.3	.053	.020	.013	.011	.006	.003
	3 (alkalinized)	93.4	.053	.026	.023	.019	.005	.003
	4 (anaerobic)	90.6	.053	.028	.026	.015	.007	.005
	5 (flooded)	94.3	.053	.023	.016	.010	.004	.003
	6 (sterilized)	90.6	.053	.0264	.021	.017	.006	.005
Chanco	1 (unamended)	90.9	.064	.035	.028	.019	.011	.005
	2 (acidified)	87.5	.064	.0314	.023	.019	.013	.008
	3 (alkalinized)	85.9	.064	.0598	.023	.018	.015	.009
	4 (anaerobic)	84.4	.064	.051	.036	.022	.016	.010
	5 (flooded)	90.6	.064	.026	.019	.014	.010	.006
	6 (sterilized)	85.9	.064	.035	.031	.021	.014	.009
Makoka	1 (unamended)	89.8	.055	.0334	.024	.018	.010	.005
	2 (acidified)	85.4	.055	.033	.021	.014	.011	.008
	3 (alkalinized)	83.6	.055	.034	.024	.017	.010	.009
	4 (anaerobic)	81.8	.055	.048	.032	.022	.016	.010
	5 (flooded)	89.1	.055	.033	.026	.014	.009	.006
	6 (sterilized)	83.6	.055	.043	.031	.020	.013	.009
Ngabu	1 (unamended)	75.7	.037	.031	.025	.019	.013	.009
	2 (acidified)	75.7	.037	.030	.025	.018	.013	.009
	3 (alkalinized)	78.4	.037	.031	.027	.013	.012	.008
	4 (anaerobic)	70.3	.037	.034	.028	.024	.016	.011
	5 (flooded)	78.4	.037	.030	.025	.017	.009	.008
	6 (sterilized)	73.0	.037	.033	.027	.021	.013	.010
Thyolo	1 (unamended)	81.9	.0276	.0216	.015	.011	.007	.005
	2 (acidified)	81.9	.0276	.0234	.014	.011	.008	.005
	3 (alkalinized)	78.3	.0276	.0192	.015	.013	.007	.006
	4 (anaerobic)	74.6	.0276	.024	.019	.014	.010	.007
	5 (flooded)	85.5	.0276	.018	.013	.009	.006	.004
	6 (sterilized)	78.3	.0276	.023	.017	.013	.009	.006

Table 23: Effect of soil treatment on degradation of metolachlor

Soil	Soil treatment	Total loss (%)	Metolachlor (µg/g) Sampling times, days					
			0	7	14	28	56	84
Bvumbwe	1(unamended)	91.0	.5329	.341	.205	.1218	.060	.048
	2 (acidified)	92.5	.5329	.318	.241	.0704	.075	.040
	3(alkalinized)	90.6	.5329	.322	.230	.080	.085	.05
	4 (anaerobic)	87.8	.5329	.496	.249	.126	.092	.065
	5 (flooded)	92.5	.5329	.449	.195	.104	.050	.040
	6 (sterilized)	87.8	.5329	.481	.2565	.124	.088	.065
Chanco	1(unamended)	87.2	.740	.531	.350	.250	.130	.0950
	2 (acidified)	89.2	.740	.550	.350	.260	.150	.080
	3(alkalinized)	89.2	.740	.560	.340	.290	.120	.080
	4 (anaerobic)	84.9	.740	.610	.430	.350	.170	.112
	5 (flooded)	90.5	.740	.470	.350	.210	.120	.070
	6 (sterilized)	85.1	.740	.580	.400	.290	.150	.110
Makoka	1(unamended)	86.3	.241	.1719	.13	.0805	.045	.033
	2 (acidified)	88.0	.241	.142	.140	.075	.043	.029
	3(alkalinized)	87.1	.241	.140	.160	.091	.041	.031
	4 (anaerobic)	84.6	.241	.201	.190	.110	.064	.037
	5 (flooded)	88.4	.241	.180	.120	.075	.038	.028
	6 (sterilized)	85.1	.241	.192	.160	.090	.050	.036
Ngabu	1(unamended)	66.7	.120	.102	.085	.068	.049	.040
	2 (acidified)	75	.120	.100	.092	.061	.051	.030
	3(alkalinized)	74.2	.120	.130	.095	.069	.061	.031
	4 (anaerobic)	64.2	.120	.180	.120	.083	.065	.043
	5 (flooded)	75	.120	.090	.071	.061	.054	.030
	6 (sterilized)	70	.120	.130	.097	.072	.062	.036
Thyolo	1(unamended)	74.3	.280	.220	.170	.130	.102	.072
	2 (acidified)	74.6	.280	.230	.160	.140	.100	.071
	3(alkalinized)	68.6	.280	.270	.180	.130	.115	.088
	4 (anaerobic)	66.1	.280	.270	.220	.180	.140	.095
	5 (flooded)	75	.280	.190	.150	.130	.095	.070
	6 (sterilized)	72.9	.280	.260	.200	.160	.120	.076

In general atrazine and metolachlor disappeared more rapidly under saturated (flooded) soil conditions. This was consistent with earlier results which indicated that saturation increases amount of herbicide in the soil solution with consequent high loss (Seybold *et al*, 2001). Soils

with higher water content show more rapid degradation of herbicides (EXTOXNET, 1996). This implies that herbicides should be applied when soils have low water content to reduce the initial fast degradation.

Sterilization of soils greatly reduced degradation of both atrazine and metolachlor, the reduction being more for metolachlor than for atrazine. This was consistent with earlier results which showed that metolachlor degraded only in unsterilized soils (Accinelli: *et al*, 2001). However in this study limited metolachlor degradation occurred in sterile soils, implying both abiotic and biotic degradation processes.

The least degradation occurred in the anaerobic (but unsaturated) soils (degradation treatment 4). This was consistent with earlier results. Research has shown that atrazine degradation is rapid at soil redox levels representing aerobic conditions and much slower at redox levels depicting anaerobic or reducing conditions Delaune *et al* (1997). Limited degradation of metolachlor under reduced (soil) conditions was expected because the formation of metolachlor OA and metolachlor ESA requires an oxidation step. These two metabolites should not form under anaerobic conditions, unless a different pathway which involves glutathione conjugation is followed (Field and Thurman, 1996). However it should be noted that in this study strict anaerobic (reduced) conditions were not maintained. This is because traces of air (hence oxygen) could have entered the incubation flasks during soil sampling and moisture correction activities.

Acidification and alkalinization of soils appeared to have no consistent effect on degradation of atrazine and metolachlor, increasing degradation (compared to unamended soil) in some and decreasing degradation in other cases (Tables 22 and 23). Best and Weber (1974) reported that atrazine degradation was more rapid at lower soil pH (5.5) than at higher pH (7.5).This was not the case in this study. This is probably because equilibration in the laboratory was not long enough for sufficient stabilization. It is strongly recommended that care should be taken when adding acids or alkalis to soils, in the laboratory, since such treatments cause changes in soil characteristics other than pH (Hamaker, 1972). However when appropriate equilibration periods are used, the practice may suffice.

4.7 Mobility of atrazine and metolachlor

4.7.1 Vertical movement of atrazine and metolachlor in packed soil columns under laboratory conditions

The vertical distributions of atrazine and metolachlor in the different soil columns are shown in Figure 21. The Bvumbwe and Chanco soils had comparatively lower residues of atrazine and metolachlor in the top three than bottom three soil layers, indicating more leaching. The Ngabu and Thyolo soils had higher herbicide residues in the top three than bottom three layers, indicating higher retention of herbicides in the surface horizons of these soils. The mobility indices and associated R_f values, based on raw data in Figure 21 (also appendix 7.2) are shown in Table 24.

Table 24: Mobility Indices (MI) and Retardation Factors (R_f) for atrazine and metolachlor in packed soil columns

Initial Moisture, %	0 (Air Dry)		5		7.5		20		Saturated			
Water input, ml	520								520		720	
	MI	R_f	MI	R_f	MI	R_f	MI	R_f	MI	R_f	MI	R_f
	Atrazine											
Bvumbwe soil	15	0.54	18	0.65	18	0.65			19	0.69	21	0.76
Chanco soil	14	0.51	15	0.54	16	0.58			17	0.62	19	0.69
Makoka soil	10	0.36	12	0.44	14	0.51			15	0.54	17	0.62
Ngabu soil	6	0.22	6	0.22			7	0.25	8	0.29	10	0.36
Thyolo soil	9	0.33	10	0.36			12	0.44	12	0.44	15	0.54
Probability	0.071								.035			
$LSD_{0.05}$	6.5								6.3			
	Metolachlor											
Bvumbwe soil	17	0.62	19	0.69	19	0.69			20	0.73	25	0.91
Chanco soil	16	0.58	17	0.62	17	0.62			19	0.69	20	0.73
Makoka soil	15	0.54	16	0.58	16	0.58			16	0.58	18	0.65
Ngabu soil	8	0.29	8	0.29			9	0.33	10	0.36	11	0.40
Thyolo soil	12	0.44	14	0.51			15	0.54	16	0.58	17	0.62
Probability	0.075								0.04			
$LSD_{0.05}$	6.5								5.8			

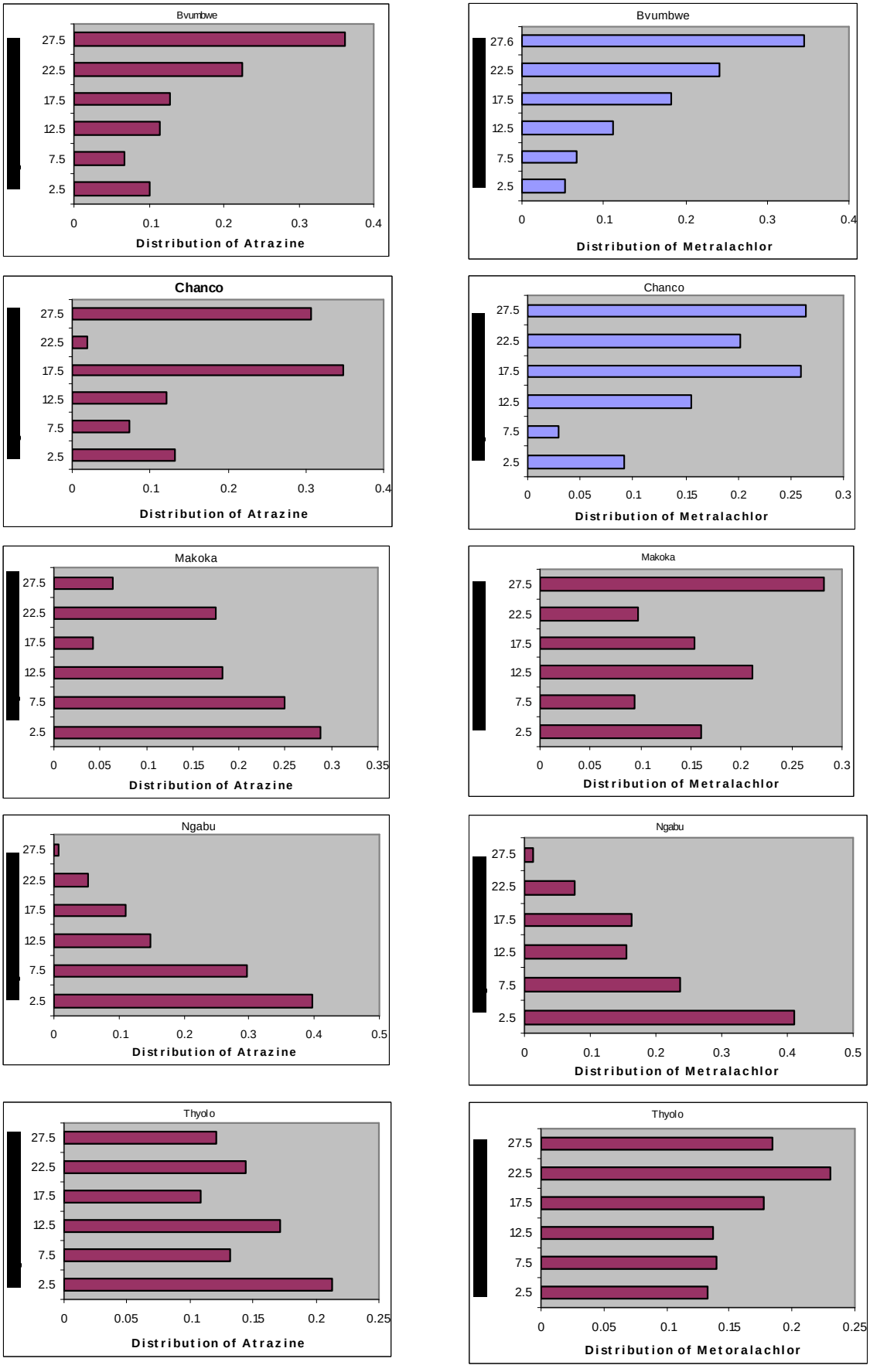


Figure 21: Vertical distribution of herbicides (µg/g) in packed soil columns

The mobilities of atrazine and metolachlor in the five soils were significantly different ($p<.035$, $p<0.040$). The order of mobility of atrazine through the five soils (saturated, with water input of 520ml) was Bvumbwe> Chanco> Makoka > Thyolo >Ngabu as determined by MI values of 19, 17, 15, 12, and 8 respectively. The order of mobility of metolachlor through the five soils (saturated, with water input of 520ml) was Bvumbwe >Chanco> Makoka=Thyolo >Ngabu as determined by MI values of 20, 19, 16, and 10 respectively. The mobilities of the two herbicides increased with increasing initial soil moisture content of the and with increasing water inputs. This can be explained by the adsorption processes. Adsorption retards the movement of most herbicides. Adsorption generally increases as the initial water content of the soils decreases. The fact that soil water significantly decreases soil's sorption affinity for herbicides was also observed by Chappell *et al* (2005). The water content of a soil can influence adsorption in two ways. Firstly, it can modify the aggregation of adsorbents and increase or decrease the accessibility of surface to solute. Secondly, water competes with herbicide molecules for Lewis acid (electron accepting) and hydrogen bonding adsorption sites on the soil and humus constituents. When soils are dry more herbicides are adsorbed hence slow leaching. When soils are moist water molecules deactivate the adsorption sites hence less herbicides are adsorbed. The unadsorbed herbicides leach easily. Higher water inputs (720 ml for the saturated soil) led to higher herbicide concentrations in the bottom three layers of all soils than lower water input (520 ml for the saturated soil). At high water fluxes, herbicides are readily dislodged hence more downward herbicide movement (Hassall, 1982).

The results of the soil column leaching studies suggest that herbicides should be applied when soils have low water content and when it is not likely to rain immediately after herbicide application in order to minimize leaching losses. Since both herbicides are mobile in all the 5 soils their effectiveness will greatly depend on the level of rainfall within the few weeks following soil application (Hassall, 1982). If rainfall is light, wash down may be insufficient to bring the chemical into contact with even shallow rooted weeds. On the other hand, if rainfall is excessive, the herbicides may be washed down to the level of the germinating crop and so become phytotoxic. For proper use of herbicides climatic conditions should be predictable. Residual pre-emergence treatment is evidently hazardous in regions where climatic conditions are unpredictable.

The Bvumbwe and Chanco soils had comparatively lower residues of atrazine and metolachlor in the top three soil layers than in the bottom three, indicating more leaching. The Ngabu and Thyolo soils had comparatively higher residues of atrazine and metolachlor in the top three soil layers than in the bottom three, indicating higher retention of herbicides in the surface horizons of these soils.

Although the mobility index of metolachlor in Thyolo soil was expected to be lower than that of Chanco soil, they had similar MI values. This could be because either some preferential flow occurred in Thyolo soil or the high water fluxes (>100 ml/day) used facilitated more downward movement of metolachlor. Metolachlor was generally more mobile than atrazine in all the five soils. This was probably due to its higher solubility. This is consistent with earlier studies on soil leaching column studies (Keller and Weber, 1995; Weber *et al*, 2003; Seybold and Mersie, 1996)

The MI values for both atrazine and metolachlor were inversely correlated with soil organic carbon (r^2 = - 0.83 for atrazine , r^2 = - 0.89 for metolachlor) contents (Table 25) as also reported in literature (Wietersen *et al*, 1993; Singh *et al*, 2002; Weber *et al* 2003 and Obrigawitch *et al*, 1981).

Table 25: Correlation coefficients for the relationship between MI and soil characteristics

Soil parameter	atrazine	metolachlor
OC	-0.83	-0.89
CEC	-0.99	-0.98
k_d	-0.99	-0.91
k_f	-0.09	-0.91
Clay	-0.84	No relationship

Leaching of herbicides through the soils decreased with increasing organic matter content of the soils. Leaching of atrazine and metolachlor was also inversely correlated with CEC (r^2 = - 0.99 for atrazine and r^2 = - 0.98 for metolachlor) and this has also been reported in literature (Weber *et al*, 2003) and soil k_d and k_f values (r^2 = - 0.99 and r^2 = - 0.98, respectively, for

atrazine and r^2 = - 0.91 and r^2 = - 0.91, respectively, for metolachlor). Atrazine mobility was also inversely correlated with clay content of the soil (r^2 = - 0.84). The residues of the two herbicides in the 0–5 cm surface soil layer (after the leaching experiment) were related to organic carbon content (r^2 = 0.88 for atrazine and r^2 = 0.91 for metolachlor), CEC (r^2 = 0.95 for atrazine and r^2 = 0.92 for metolachlor) and clay content (r^2 = 0.82 for atrazine only) of the soils.

4.7.2 Vertical and horizontal movement of atrazine and metolachlor in the field

4.7.2.1 Vertical movement of herbicides

The vertical movement data for atrazine and metolachlor is shown in Table 26.

The results revealed that fourteen days after application of atrazine and exposure to 135.8 mm and 76.5 mm rain at Chanco and Bvumbwe, respectively, atrazine was detected in the 20 – 25 cm layer of the soil profiles at both Chancellor College and Bvumbwe.

Fourteen days after application of metolachlor and exposure to 53.7 mm and 76.5 mm rain at Chanco and Bvumbwe, respectively, metolachlor was also detected in the 20 - 25 cm layer of the soil profiles at both Chancellor College and Bvumbwe. Five weeks after herbicide application, 0.03-0.63% of the initial concentrations of atrazine and metolachlor at day 0 was located at the 40 cm depth in both soil profiles.

There was consistent decrease in pesticide residue concentration in the 0 - 5 cm soil layer with time after spraying. This was probably due to herbicidal action, leaching, microbial and chemical (including photochemical) degradation and volatilization (Guenzi, 1974; Cheng, 1990). In the 2 - 25 cm depth herbicide concentration increased with time as leaching occurred and then decreased with time as further leaching and dissipation occurred. After 210 days no herbicides were detected in the 0 - 25 cm soil profile.

Table 26: Percent (%) herbicide in soil, with day 0 as reference point

	Herbicide incorporated into soil					Herbicide on soil surface				
Depth, cm	0-2	2-5	5-10	10-15	15-25	0-2	2-5	5-10	10-15	15-25
	Atrazine, Chanco									
0Day	67	33	0*	0	0	100	0	0	0	0
2Weeks	10	11	15	14	7	16	9	15	15	5
5Weeks	7	6	6	8	9	9	13	9	5	4
30Weeks	0	0	0	0	0	0	0	0	0	0
	Atrazine, Bvumbwe									
0Day	70	30	0	0	0	100	0	0	0	0
2Weeks	8	10	13	13	10	12	6	12	14	10
5Weeks	5	8	5	7	10	10	7	4	3	10
30Weeks	0	0	0	0	0	0	0	0	0	0
	Metolachlor, Chanco									
0Day	65	35	0	0	0	100	0	0	0	0
2 weeks	20	20	12	8	2	25	20	10	6	1
5 weeks	7	8	6	15	5	8	20	6	14	5
12 weeks	0	1	2	2	2	0	8	1	2	1
30 weeks	0	0	0	0	0	0	1	0	0	0
	Metolachlor, Bvumbwe									
	63	37	0	0	0	100	0	0	0	0
2 weeks	11	10	10	17	19	14	9	10	15	17
5 weeks	3	4	17	19	16	5	4	15	18	17
12 weeks	0	0	0	0	7	0	0	0	1	5
30 weeks	0	0	0	0	0	0	0	0	0	0

0 value means atrazine or metolachlor, if present, were below the detection limit

The trends in mobility of atrazine and metolachlor are shown in Figures 22a and 22b, respectively.

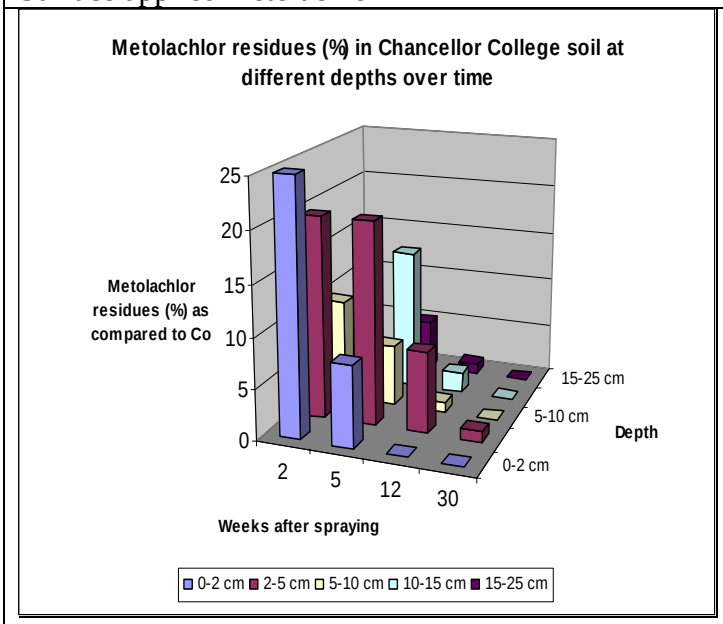
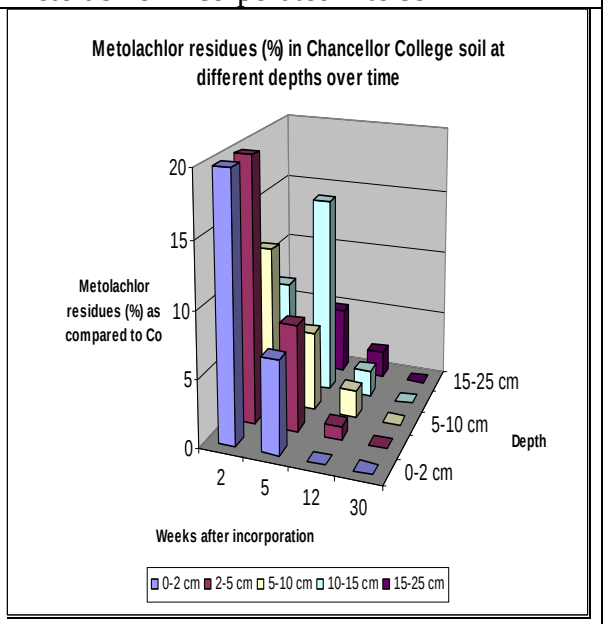
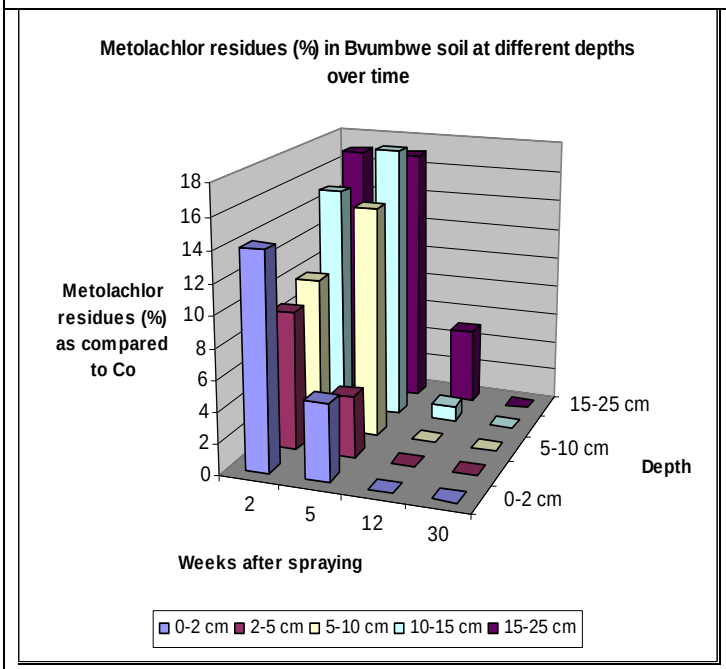
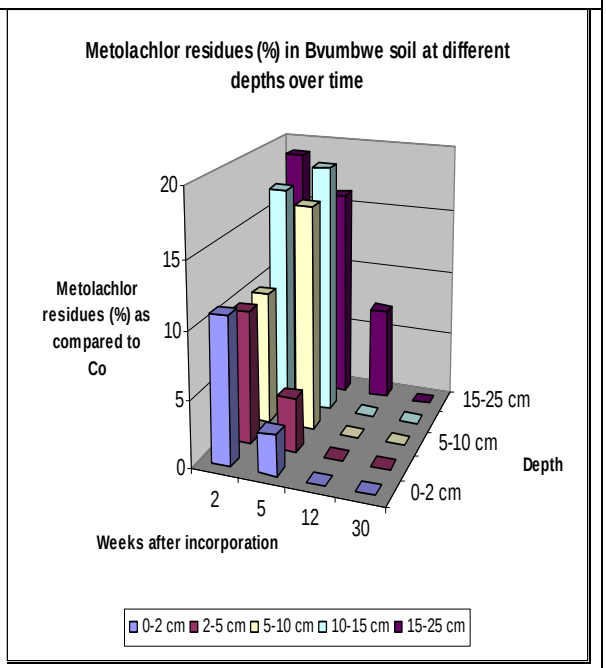
Surface applied metolachlor	Metolachlor incorporated into soil
	
	

Figure 22a: Metolachlor residues (%) in soils (field) at different depths over time. Co is the initial metolachlor concentration on day 0

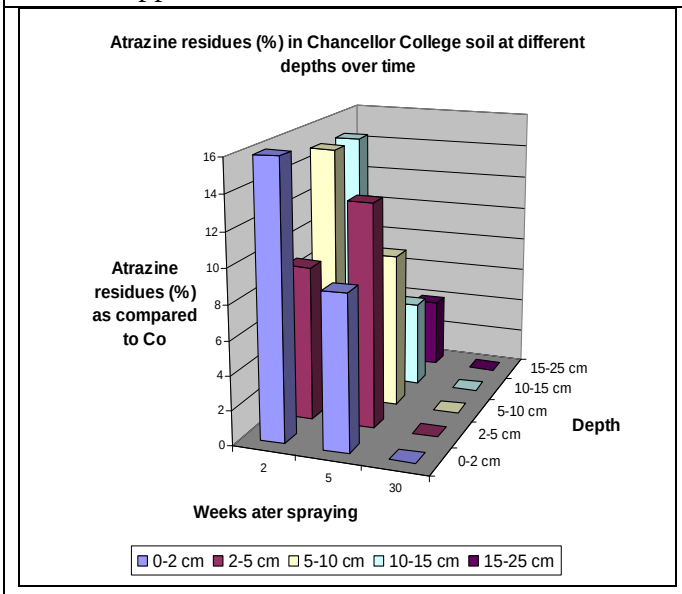
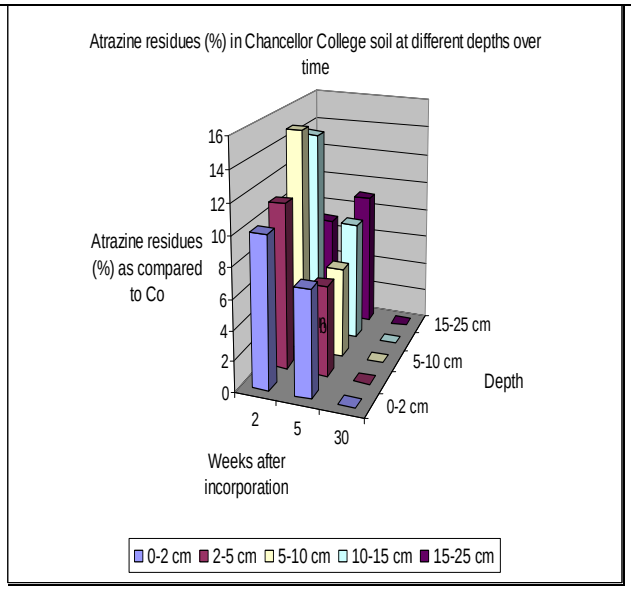
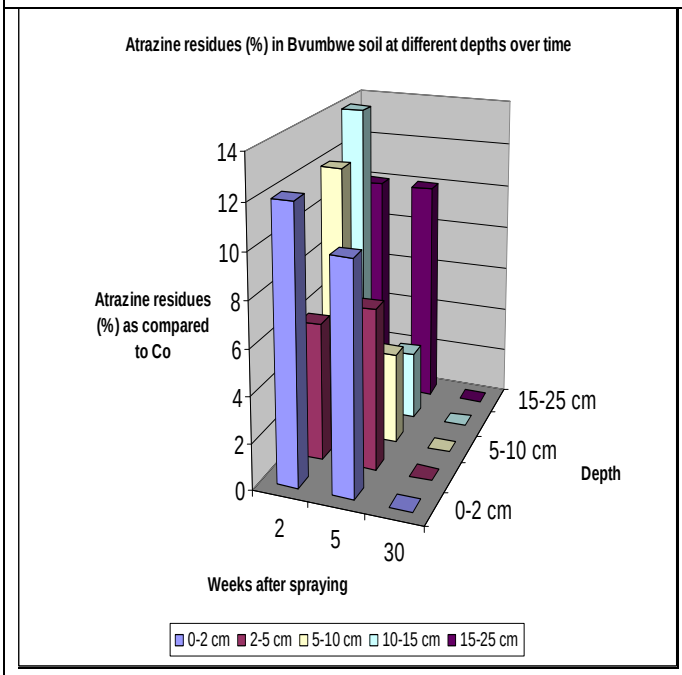
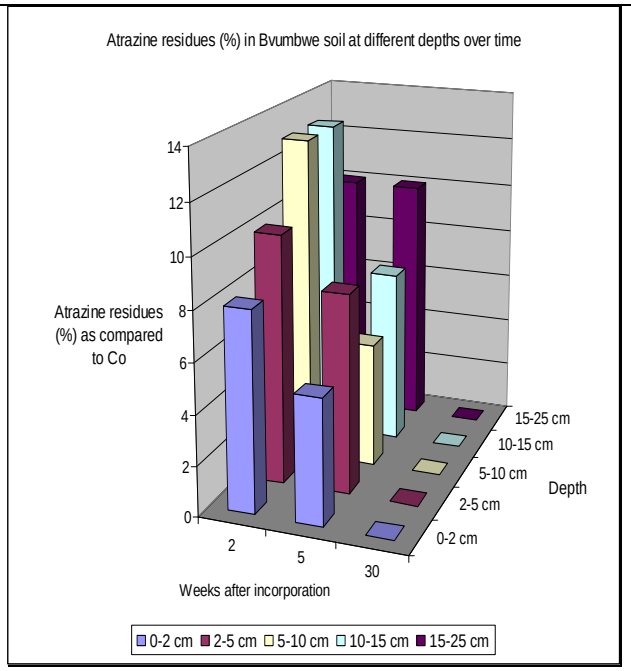
Surface applied atrazine	Atrazine incorporated into soil
	
	

Figure 22b: Atrazine residues (%) in soils (field) at different depths over time. Co is the initial atrazine concentration on day 0

The mobility indices for the two herbicides under field conditions are shown in Table 27.

Table 27: Mobility Index values (MI) for the two herbicides under field conditions

Time after herbicide application	Soil	Herbicide incorporated Into soil		Herbicide on soil surface	
		Atrazine	Metolachlor	Atrazine	Metolachlor
2 weeks	Bvumbwe	9.3	10.6	8.1	10.0
	Chanco	8.4	5.2	8.3	4.3
5 weeks	Bvumbwe	10.3	11.9	8.8	11.8
	Chanco	9.7	9.0	6.5	7.5

The data in Tables 26 and 27 (and trends in Figures 22a and 22b) indicate that incorporation of herbicides facilitated downward movement of herbicides (especially in the Chanco soil) and that herbicides were generally more mobile in the Bvumbwe soil than in the Chanco soil. Bvumbwe soils have lower clay and organic carbon contents than Chanco soils (Table 10). Research has shown that mobility of metolachlor is inversely related to soil clay and organic matter contents (Obrigawitch *et al*, 1981). In addition, more rain at Bvumbwe (418.2 mm) than at Chanco (236.8 mm for atrazine and 154.7 mm for metolachlor) accelerated leaching at Bvumbwe.

For the Bvumbwe and Chanco soils (5 weeks after herbicide application) metolachlor was more mobile than atrazine. This was because of metolachlor's higher solubility (solubility of atrazine and metolachlor is 33 and 530 mg/l, respectively). Keller and Weber (1995) also established that metolachlor was more mobile than atrazine. For the Chancellor College soil, two weeks after herbicide application, atrazine was unexpectedly more mobile than metolachlor. Since k_d values for atrazine and metolachlor were nearly similar, mobility would mostly depend on water solubility. The higher mobility of atrazine may have been due to heterogeneously distributed preferential flow pathways in the Chanco soil on which atrazine was applied (Hance, 1980; Laabs *et al*, 2002). These preferential flow pathways may have disappeared with time.

4.7.2.2 Horizontal movement of herbicides

The horizontal movement of atrazine is shown in Table 28.

Table 28: Atrazine in soil (µg/g) at different distances (after two weeks of atrazine application)

Distance from point of application (metres)	Chanco		Bvumbwe	
0.5	Atrazine on soil surface	Atrazine incorporated into soil	Atrazine on soil surface	Atrazine incorporated into soil
1	0.0028	0.0045	0.0021	0.0019
5	0.0019	0.0030	0.0013	0.0011
10	0.0010	0.0011	0	0
≥20	0	0	0	0

Horizontal movement of herbicides occurred on all plots. Some surface run off herbicide losses was expected. A review of experimental studies of pesticide leaching indicated that <0.005 to 5.43% of applied mass of herbicides is lost through surface run off (Flury, 1996). The surface run off deposits herbicides on the soils over which the run off is passing. At Bvumbwe there was more horizontal atrazine movement from plots with surface applied atrazine than from the plots where atrazine was incorporated into the soil, although the differences were not statistically significant. Soil herbicide residues that are picked up in a run off event come from a soil layer possibly as thin as 2 - 3 mm (Ahuja, 1982; Ahuja *et al*, 1981). If herbicides are left on the surface this layer has higher herbicide concentration than when the same quantities of herbicides are incorporated into the soil. A run off event would therefore pick up more herbicides from plots with surface application than from plots with incorporated herbicides. However, at Chancellor College, horizontal atrazine movement was higher from plots with incorporated atrazine than from plots with surface applied atrazine. Rain (82.1mm) fell soon after the herbicide was applied. Since incorporation loosened the top soil more soil erosion occurred, leading to more herbicide run off. This result shows that it is

important to predict weather conditions. Herbicides should be applied only when it is likely not to rain soon after herbicide application. According to Sasakawa Global 2000 MW herbicides should be applied when it is likely not to rain in the next six hours after herbicide application (Jose *et al*, 2005 and Chitowe, personal communication). A storm soon after pesticide application may cause very high pesticide losses (up to 17% of applied atrazine mass) to surface waters (Wauchope, 1978).

Generally, more atrazine ran off at Chancellor College than at Bvumbwe. This was because the Bvumbwe soil had a coarser texture than the Chancellor College soil hence it had more infiltration than run off. In addition, herbicide application was immediately followed by lighter rain at Bvumbwe (5.2 mm) than at Chancellor College (82.1 mm) (Table 37 in appendix 3).

4.7.2.3 Groundwater contamination potential (GWCP)

The leaching potential of the soils (SLP) is given in Table 29. Considering the SLP indices, Bvumbwe soil (with the least organic matter and clay) had the highest whilst Ngabu soil (with the highest organic matter and high clay) had the least leaching potential. According to the SLP rating system reported by Murphy (2006) Ngabu and Thyolo soils had low, Makoka soil had medium and Bvumbwe and Chancellor College soils had high leaching potentials.

Table 29: SLP rating categories

Soil	Organic matter		Texture (Murphy, 2006)		pH		SLP index	SLP rating category (Murphy, 2006) High >131; Moderate 90 – 130; Low <89
	rating	factor	rating	factor	rating	factor		
Bvumbwe	8	10	10	6	2	3	146	High
Chanco	7	10	10	6	3	3	139	High
Makoka	8	10	6	6	3	3	125	Moderate
Ngabu	1	10	1	6	6	3	34	Low
Thyolo	7	10	1	6	3	3	85	Low

The herbicide leaching potentials are shown in Table 30.

The herbicide leaching potential indices show that metolachlor had higher leaching potential than atrazine in all soils, probably because of its higher solubility, higher application rate and slightly higher half-life. The higher the half-life of an herbicide the more likely it is to leach to groundwater. The herbicide leaching potential indices also show that the leaching potentials of both herbicides were least in Ngabu soil but very high in Bvumbwe soil.

Table 30: Herbicide leaching potential (HLP) rating categories

Soil	Herbicide leaching Potential			
	Atrazine		Metolachlor	
	R = 0.9 kg/Ha^r (0.816 lbs/acre^r)		R = 1.44 kg/Ha^r (1.306lbs/acre^r)	
	F = 1		F = 1	
	HLP Index	Rating Category (Murphy, 2006)	HLP Index	Rating Category (Murphy, 2006)
Bvumbwe	22.8	High	41.6	High
Chancellor College	19.6	High	37.0	High
Makoka	19.7	High	41.9	High
Ngabu	15.8	High	28.6	High
Thyolo	17.0	High	39.7	high

^{r} average (recommended) herbicide application rate used by farmers

Groundwater contamination potential ratings, based on SLP and HLP indices in Tables 29 and 30, of the herbicide-soil system are shown in Table 31.

Table 31: GWCP rating

Soil	Herbicide	
	atrazine	Metolachlor
Bvumbwe	Very high risk	Very high risk
Chanco	Very high risk	Very high risk
Makoka	High risk	High risk
Ngabu	Moderate risk	Moderate risk
Thyolo	Moderate risk	Moderate risk

The results showed that the groundwater contamination potential of the herbicide–soil system was in the order Bvumbwe, Chancellor College>Makoka>Thyolo, Ngabu. This was consistent with the sorption coefficients and organic matter and clay contents of the soils. Soils with higher clay and organic matter contents should have less groundwater contamination potential since clay and organic matter retard herbicide movement. The groundwater contamination potential for metolachlor was higher than that of atrazine. This was consistent with the higher solubility and application rates of the herbicides.

4.7.2.4 Simulation of herbicide movement by the PEARL model

The predictions for herbicide concentrations in the soil profiles were not successful. The predicted values were different from the observed results, probably due to subjectivity in the model input data. Boesten (2000) reported that the major source of differences in model results is the subjectivity in the derivation of model inputs. In this case the differences could be due to the inadequate weather data. The PEARL model requires daily global radiation, minimum and maximum temperatures, average vapour pressure, average wind speed, rain and reference evapotranspiration for a period of 20 years. The meteorological department had no daily average vapour pressure data. It also had no daily global radiation values, only monthly global radiation values. The global radiation data input, therefore, comprised the same estimated daily value for all days in a month. Daily data for the other variables was available but with a lot of gaps.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study has shown that the soils were significantly different in adsorption of atrazine and metolachlor, Ngabu soil being more effective while Bvumbwe soil being the least. Generally, the order of adsorption for atrazine was Ngabu > Thyolo > Makoka > Chanco > Bvumbwe. In the case of metolachlor the order of adsorption was Ngabu > Thyolo > Chanco > Makoka > Bvumbwe. The adsorption of the two herbicides were consistent with all adsorption isotherms (Freundlich, r^2 = 0.96 - 0.99, Linear, r^2 = 0.90 - 0.99, Langmuir r^2 = 0.80 - 0.96 and Temkin, r^2 = 0.94 - 0.99). Clearly, adsorption of atrazine and metolachlor followed the order: Freundlich > Temkin > Linear > Langmuir. Adsorption of atrazine and metolachlor (k_d) significantly correlated with organic carbon (r = 0.88 for atrazine and r 0.99 for metolachlor) and cation exchange capacity (r = 0.98 for atrazine and r=0.89 for metolachlor) and pH (r = 0.88 for atrazine and r=0.94 for metolachlor). The relationship between sorption coefficients and clay content was variable, being significant for atrazine (r = 0.81) but not significant for metolachlor.

Desorption from soils was hysteric in all cases, being more irreversible at the lowest adsorbed herbicide concentrations. Consequently, low herbicide dosages would not be effective. The Ngabu soil exhibited least desorption percentages. Consequently, the Ngabu soil would require higher herbicide dosages than the other soils for same herbicidal activity.

The results showed significant differences ($p<0.01$, $p<0.002$) in the degradation of the two herbicides in the soils, with laboratory SFO half-lives ranging from 22 to 43 days for atrazine and 25 to 54 days for metolachlor. The first order degradation of atrazine and metolachlor were consistent with degradation models (SFO, r^2 = 0.95 - 0.99; DFOP, r^2 = 0.97 - 0.99 and HS, r^2 = 0.91 – 0.99, respectively). The degradation of the two herbicides followed the order DFOP>SFO>HS.

Half-lives for both atrazine and metolachlor were significantly correlated with adsorption coefficients (r^2= 0.99 for atrazine and r^2 = 0.87 for metolachlor), clay (r^2= 0.88 for atrazine and r^2 = 0.92 for metolachlor) and organic matter (r^2= 0.83 for atrazine and r^2 = 0.77 for metolachlor) contents of the soils. Herbicides persisted longer in soils with higher organic

matter and clay contents. Degradation was faster in saturated (flooded) soils but slower in sterilized soils and in unsaturated soils with very low or no oxygen.

The mobility of herbicides was affected by the intensity of herbicide adsorption by soil constituents (k_d), solubility of the herbicide in water, initial soil water content at the time of herbicide application, the level of water input after herbicide application and herbicide longevity (half life). The leaching of herbicides was inversely related to soil k_d and k_f values (r^2 = - 0.99*** and r^2 = - 0.98*** respectively for atrazine and r^2 = - 0.91*** and r^2 = - 0.91*** respectively for metolachlor), decreasing with increasing cation exchange capacity, and organic carbon and clay contents of the soils. The mobility of atrazine and metolachlor increased as water input and initial soil moisture content increased. Mobility index (MI) values showed that leaching of the two herbicides followed the order Bvumbwe>Chancellor College>Makoka>Thyolo>Ngabu. This order was confirmed by the groundwater contamination potential (GWCP) ratings derived using the simple decision aid model. The vertical movement of herbicides, under field conditions, revealed some preferential flow in the Chanco soil. Horizontal movement of atrazine was affected by soil texture, amount and timing of rainfall after herbicide application and herbicide placement method. It was reduced by incorporating the herbicides into the top 3cm of soil.

The results suggest that herbicides should be applied when soils are neither too dry nor too wet and when it is not likely to rain immediately after herbicide application.

Atrazine was detected in 38% whilst metolachlor was detected in 15% of the surface water samples. The highest herbicide concentrations in surface waters occurred following the first run off events after herbicide application and decreased with time, decreasing to zero by the twelfth week. The concentrations were generally below the WHO recommended maximum guideline values. The contamination depended mainly on land husbandry practices. Soils with lower organic matter and clay contents are relatively more prone to herbicide leaching. These may have higher risk of ground water contamination by atrazine and metolachlor. Soils with high organic matter and clay contents are relatively more prone to herbicide run off if soil erosion occurs. These may have higher risk of surface water contamination by atrazine and metolachlor.

5.2 Recommendations

It is recommended that further research is undertaken to

i. Assess the effect of herbicide incorporation in clay soils on herbicidal activity,
ii. Establish the sorption of herbicides in soils having relatively low water contents (not saturated soils as in this study) and assess degradation at different temperatures, and.
iii. Identify areas that have significant potential for off site herbicide movement, so we can work there first to maximize environmental risk mitigation with our limited resources.

In order to reduce export of herbicides to water bodies it is recommended to maintain high organic matter in soils, incorporate herbicides into high clay soils, avoid spraying when soils are too dry or too wet, base herbicide dosages on clay mineralogy of the soil (in addition to clay content and crop type) and maintain a percentage of the farm area as an herbicide filtering area. Field staff and agricultural producers should be educated on the influence of soil and herbicide properties on the fate of herbicides in the environment.

Weather data is necessary for herbicide movement simulation models. The Department of Meteorological Services should address all weather data issues.

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APPENDICES

1 Raw sorption data for atrazine and metolachlor

Table 32: Adsorption data for atrazine

Soil		Initial concentration of atrazine solution, µg/ml						
		0.5	1	2	2.5	3	4	5
Thyolo	Ce µg/ml	0.3	0.65		1.7			3.9
	Cs µg/g	1	1.75		4			5.37
Ngabu	Ce µg/ml	0.25	0.6	1.2	1.55		2.85	
	Cs µg/g	1.25	2	3.99	4.75		5.63	
Makoka	Ce µg/ml	0.32	0.76	1.55		2.38	3.25	
	Cs µg/g	0.86	1.17	2.2		3.12	3.64	
Bvumbwe	Ce µg/ml	0.36	0.8	1.7	2.05	2.55	3.45	
	Cs µg/g	0.72	0.97	1.46	1.25	2.18	2.7	
Chanco	Ce µg/ml	0.35	0.75	1.55	1.98	2.38	3.3	
	Cs µg/g	0.72	1.24	2.21	2.6	3.02	3.35	

Table 33: Adsorption data for metolachlor

		Initial concentration of metolachlor solution, µg/ml					
Soil		0.5	1	2	3	4	5
Thyolo	Ce µg/ml	0.30	0.70	1.45	2.20	2.95	
	Cs µg/g	0.99	1.50	2.73	3.97	5.21	
Ngabu	Ce µg/ml	0.18	0.51	1.20	1.79	2.50	3.20
	Cs µg/g	1.62	2.41	3.99	6.00	7.44	8.97
Makoka	Ce µg/ml	0.35	0.75	1.58	2.45	3.35	4.25
	Cs µg/g	0.74	1.24	2.06	2.74	3.19	3.67
Bvumbwe	Ce µg/ml	0.37	0.77	1.60	2.45	3.43	
	Cs µg/g	0.65	1.11	1.95	2.66	2.86	
Chanco	Ce µg/ml	0.34	0.70	1.42	2.39	3.35	4.28
	Cs µg/g	0.79	1.49	2.82	3.03	3.22	3.61

Table 34: Mass of soil used in sorption studies

Soil	Atrazine							Metolachlor					
	Initial concentration of atrazine solution, µg/ml							Initial concentration of metolachlor solution, µg/ml					
	0.5	1	2	2.5	3	4	5	0.5	1	2	3	4	5
Thyolo	1.034	1.034	1.073	1.00	1.040	1.021	1.024	1.012	1.000	1.008	1.010	1.007	1.009
Ngabu	1.046	1.027	1.009	1.00	1.031	1.022	1.039	1.004	1.018	1.003	1.009	1.008	1.003
Makoka	1.028	1.028	1.015	1.00	1.032	1.031	1.014	1.020	1.012	1.021	1.005	1.019	1.021
Bvumbwe	1.031	1.013	1.015	1.00	1.078	1.020	1.050	1.003	1.036	1.025	1.034	1.005	1.026
Chanco	1.044	1.046	1.026	1.00	1.035	1.043	1.064	1.009	1.004	1.018	1.008	1.009	1.003

2 Raw mobility data for atrazine and metolachlor

Table 35: Mobility of atrazine data (µg/g)

Soil	Depth (cm)	Initial moisture content of soil (%)				
		0	5	7.5 (20 for Ngabu, Thyolo)	Saturated	Saturated
		Water input (ml)				
		520	520	520	529	720
Bvumbwe	2.5	.153	.051	.071	.102	0
	7.5	.141	.066	.134	.067	.064
	12.5	.120	.148	.162	.115	.080
	17.5	.259	.436	.157	.129	.084
	22.5	.193	.135	.220	.225	.526
	27.5	.132	.162	.256	.362	.246
Chanco	2.5	.178	.055	.110	.132	.028
	7.5	.212	.097	.147	.073	.090
	12.5	.161	.458	.167	.120	.164
	17.5	.144	.127	.207	.349	.205
	22.5	.136	.123	.161	.019	.274
	27.5	.169	.140	.209	.307	.240
Makoka	2.5	.360	.253	.166	.288	.020
	7.5	.233	.164	.182	.249	.163
	12.5	.233	.162	.152	.182	.218
	17.5	.015	.307	.209	.042	.262
	22.5	.009	.065	.176	.175	.073
	27.5	.151	.049	.115	.063	.263
Ngabu	2.5	.723	.612	.463	.386	.231
	7.5	.035	.216	.346	.297	.357
	12.5	.060	.045	.050	.148	.145
	17.5	.060	.046	.051	.111	.154
	22.5	.050	.042	.051	.052	.070
	27.5	.072	.039	.039	.007	.043
Thyolo	2.5	.212	.322	.190	.213	.136
	7.5	.405	.214	.254	.132	.186
	12.5	.255	.177	.278	.172	.139
	17.5	.048	.170	.120	.109	.230
	22.5	.060	.057	.071	.144	.171
	27.5	.020	.059	.088	.121	.138

Table 36: Mobility of metolachlor data (µg/g)

Soil	Depth (cm)	Initial moisture content of soil (%)				
		0	5	7.5 (20 for Ngabu and Thyolo)	Saturated	Saturated
		Water input (ml)				
		520	520	520	520	720
Bvumbwe	2.5	.026	.018	.009	.052	0
	7.5	.064	.092	.080	.067	0
	12.5	.335	.228	.221	.111	.010
	17.5	.276	.198	.168	.183	.021
	22.5	.232	.391	.327	.241	.325
	27.5	.067	.104	.194	.345	.644
Chanco	2.5	.061	.044	.111	.092	0
	7.5	.094	.094	.155	.029	.121
	12.5	.288	.272	.119	.155	.315
	17.5	.220	.209	.234	.259	.321
	22.5	.210	.237	.171	.202	.174
	27.5	.126	.143	.209	.264	.068
Makoka	2.5	.173	.158	.243	.160	.104
	7.5	.152	.180	.065	.094	.132
	12.5	.112	.118	.170	.211	.108
	17.5	.112	.093	.117	.153	.188
	22.5	.174	.156	.088	.098	.212
	27.5	.275	.294	.316	.282	.255
Ngabu	2.5	.409	.370	.290	.410	.301
	7.5	.313	.330	.326	.238	.170
	12.5	.170	.142	.193	.106	.135
	17.5	.069	.087	.098	.162	.258
	22.5	.032	.059	.065	.075	..123
	27.5	.007	.011	.027	.009	..013
Thyolo	2.5	.190	.143	.158	.132	.055
	7.5	.322	.291	.193	.140	.171
	12.5	.155	.123	.172	.137	.218
	17.5	.985	.059	.153	.177	.124
	22.5	.180	.295	.193	.230	.218
	27.5	.067	.089	.130	.184	.215

3 Rainfall data

Table 37: Rainfall (mm) at Bvumbwe and Chanco

Days after application	Bvumbwe	Chanco*	
	atrazine and metolachlor	atrazine	metolachlor
0-1	5.2	82.1	6.1
1-7	28.4	27.2	37
7-15	42.9	26.5	10.6
15-30	140.5	41.9	41.9
30-60	176.6	57.6	57.6
60-90	24.6	1.5	1.5
Total (0-90)	418.2	236.8	154.7

* Atrazine and metolachlor were applied on different days at Chanco.

4 Analytical methods for soil characterization (Source: Bvumbwe Agricultural Research Station)

4.1 Determination of aluminium

Reagents:

Potassium chloride, KCl, (1.0N): 37.275g in 500 ml de-ionized water.

Potassium fluoride, KF, (1.0N): 29.05g in 500 ml de-ionized water.150

Sulphuric acid, H_2SO_4, (0.1N) standard solution: 2.452g in 500 ml de-ionized water.

Sodium hydroxide, NaOH, (0.1N) standard solution: 2.00g in 500 ml de-ionized water.

Phenolphthalein indicator (0.1%)

Procedure:

Weigh 10g soil sample into 250 ml beaker and add 50 ml of 1.0N KCl.

Mix several times and let stand for 30 minutes. Filter through Whatman No. 42 filter paper. Leach each sample as rapidly as possible with about 9 ml of KCl.

Transfer the filtrate to 100 ml volumetric flask and make to the mark with 1.0N KCl solution and transfer to a conical flask.

Add 6 to 8 drops of the indicator and titrate with standard 0.1N NaOH standard solution to a pink colour (V1).

Add 10 ml of potassium fluoride and titrate with standard 0.1N sulphuric acid until pink colour disappears.

Add more indicator if there is more aluminium in the sample and continue titrating to colourless end point (V2).

Run blank determinations:

(i) Titrate 100 ml 1.0N KCl with 0.1N NaOH (Vb_1).

(i) Titrate 10 ml 0.1N KF with 0.1N H_2SO_4 (Vb_2)

Calculations:

$$\text{Extractable acidity (meq/100g)} = \frac{(V1 - Vb_1) \times 0.1}{10} \times 100$$

$$\text{Aluminium (meq/100g)} = \frac{(V2 - Vb_2) \times 0.1}{10} \times 100$$

Equations

$2Al^{3+} + 3Cl_2 \rightarrow 2AlCl_3$

$HCl + NaOH \rightarrow H_2O + HCl$

$AlCl_3 + 3NaOH \rightarrow Al(OH)_3 + 3NaCl$

$Al(OH)_3 + 6KF \rightarrow 3KOH + K_3AlF_6$

$KOH + H_2SO_4 \rightarrow K_2SO_4 + H_2O$

4.2 Determination of total organic carbon (Walkley-Black Method)

Reagents:

1. 1N Potassium dichromate solution: Dissolve 49.04 g AR Potassium dichromate ($K_2Cr_2O_7$) in de-ionized water and make up to I litre. Some warming is usually necessary to complete solution. Allow to cool before finally making up to volume.
2. 0.5N Ferrous ammonium sulphate solution: Dissolve 196 g Ferrous ammonium sulphate {Fe (NH4) 2(SO4) 2} in water. Add 5 ml concentrated sulphuric acid and make up to I litre with distilled water. An alternative reagent is ferrous sulphate (139g/litre)
3. Diphenylamine indicator solution: dissolve 0.5 g diphenylamine in a mixture of 100 ml concentrated sulphuric acid and 20 ml distilled water.
4. Concentrated Sulphuric acid (98%).
5. Concentrated Phosphoric acid (85-90%).

Procedure:

1. Weigh out 1.00 g soil into a 500 ml conical flask. Include one flask for a blank.
2. Add 10.0 ml 1 N potassium dichromate solution with a pipette.
3. Gently add 15 ml concentrated sulphuric acid and shake for 1 minute and stand for 30 minutes to allow complete oxidation to take place.
4. Add 150 ml distilled water and 5 ml concentrated phosphoric-acid and allow the solution to cool.
5. Add 1 ml diphenylamine indicator and immediately titrate against 0.5 N Ferrous ammonium sulphate until the colour changes from deep blue to dark green.

NB: The volume of ferrous ammonium sulphate added is equivalent to the quantity of potassium dichromate not used by the soil. Carry blank determination through exactly as described above, now omitting the soil.

Calculation:

To find the concentration of ferrous ammonium sulphate

$$N_1V_1(\ K_2Cr_2O_7\ ) = N_2V_2Fe(\ NH_4\ )_2(\ SO_4\ )_2$$

$$N_2 = \frac{N_1 V_1}{V_2}$$

The volume of potassium dichromate used in the soil $V_s = (V_{blank} - V_2)$.

%C in the sample given 1 ml 1 N $K_2Cr_20_7$ reacts with 0.003 g C

$$\%C = \frac{V_S N_2 \times 0.003 \times 100 \times 1.33}{W}$$

%OM = %C X 1.774

where W = weight of soil used N_1 and V_1 = normality and volume of potassium dichromate respectively. N_2 and V_2 = normality and volume of ferrous ammonium sulphate respectively, and V_{blank} = Volume of ammonium ferrous sulphate used in the blank

4.3 Determination of total nitrogen

Reagents:

1. Mixed catalyst: Weigh accurately and mix 160 g anhydrous potassium sulphate (or sodium sulphate), 10 g cupric sulphate ($CuS0_4.5H_20$) and 3 g selenium powder.
2. Sodium Hydroxide: 46% solution. Dissolve 460 g NaOH in a litre of distilled water.
3. 2% Boric acid: dissolve 2 g H_3B0_3 in 100 ml hot de-ionized water.
4. Mixed indicator: dissolve 0.15g bromocresol green and 0.1 g methyl red in 250 ml 90% ethanol.
5. Sodium carbonate, Na_2CO_3, solution (0.25N): 13.50g in 1 litre of distilled water
6. N/70 (0.15) Hydrochloric acid:

(a) Dilute 12.5 ml AR concentrated hydrochloric acid to I litre with distilled water. This solution will be about 0.15 N HCl.

(b) Titrate 20 ml of 0.25 N sodium carbonate solution against this acid solution, using the methyl orange indicator. Include a blank and correct for this.

Let the titre be P ml.

(c) Dilute $\frac{20}{7}P$ (2.857×P) ml of the 0.15 N acid solution to 1 litre to give N/70 hydrochloric acid.

Digestion:

1. Accurately weigh 1.0 g soil sample into Kjeldahl flask, moisten the soil with 1.5 ml distilled water and allow the flask stand for 30 minutes.
2. Add 1.7 g mixed catalyst followed by 5.0 ml conc. sulphuric acid. Digest the sample beginning at low heat for about 10 minutes and then increase the heat and continue digesting until the colour changes to pale green, shaking at intervals. Continue digesting for I hour after colour change.
3. Allow the flask to cool and then add 10 ml distilled water. When cool decant the solution into 50 ml volumetric flask leaving behind the sand, wash the sand, several times using 10 ml distilled water each time and decanting the washings into the 50 ml volumetric flask and finally make the volume to the mark with distilled water.

Distillation:

1. Pipette 10 ml aliquot of the solution into Markham still, add 5.0 ml of 46% NaOH through the funnel of the still while the stop rod is in position then lift the stop rod to allow the solution to flow into the still, wash the funnel with 10 ml distilled water.
2. Steam distil, collecting the distillate in 50 ml conical flask containing 5.0 ml of 2% Boric acid to which 5 drops of mixed indicator is added. Distil till colour turns green. Continue distilling for I minute after colour change.

Titration:

Titrate the distillate with standardized N/70 HC1 until the colour changes to whine red. Record the volume of the titre (V_1).

Calculation:

The 10 ml aliquot is equivalent to 0.2g of soil taken. Given that 1.0 ml of N/70 HCI = 0.2mg Nitrogen

$$\%N = \frac{V_1 \times 0.2mg \times 100}{0.2g}$$

$$\%N = \frac{V_1}{10}$$

4.4 Extraction of P, Na, K, Mg and Ca (Mehlich 111 method)

Reagents:

I. Acetic acid (0.2M)

2. Ammonium Nitrate (0.25 M)

3. Ammonium Fluoride (0.0 15 M)

4. Nitric acid (0.013 M)

5. Ethylene diamine tetra acetic acid (EDTA) (0.00 I M)

Preparation:

1. First prepare the ammonium fluoride-EDTA stock reagent by dissolving 138.9 g of ammonium fluoride (NH_4F) and 73.5g and EDTA in 1 litre distilled water.

2. To prepare 4 litres Mehlich 111 extracting reagent, weigh 80g ammonium nitrate (NH_4NO_3) into 3000 ml distilled water and add 16 ml ammonium fluoride-EDTA stock prepared above, and then add 46 ml acetic acid and 3.28 ml concentrated nitric acid. Adjust the pH to 2.0 ± 0. 1 and bring the final volume to 4 litres with distilled water.

Extraction Procedure:

1. Scoop 2.5 cm^3 soil into extracting polythene bottle.

2. Add 25 cm^3 Mehlich 3 Extractant.

3. Vigorously shake the soil with the Extractant for 5 minutes.

4. Filter and save the filtrate.

5. The extract is ready for elemental P, K, Na, Ca and Mg determination.

4.4.1 Detection of Cations (K, Ca, Mg, and Na*)*

Preparation of Standard solutions:

(a) Stock Solution for calcium, magnesium, potassium and sodium.

Calcium: 1000mg/l

Dissolve 2.4973 g calcium carbonate in 25 ml of I M hydrochloric acid and dilute to 1 litre with distilled water; or dissolve 2.7693 g of calcium chloride in 100 ml of distilled water and dilute to 1 litre. Store in a polythene bottle.

Magnesium: 1000 mg/l

Dissolve 1.000 mg magnesium metal in 50 ml of 5 M hydrochloric acid and dilute to 1 litre in a volumetric flask with distilled water. Store in a polythene bottle.

Potassium: 1000 mg/l

Dissolve 1.9070 g of dry potassium chloride in distilled water. Dilute to I litre in a volumetric flask with distilled water. Store in a polythene bottle.

Sodium: 1000mg/l

Dissolve 3.6973g of dry sodium carbonate in distilled water and dilute to 1 litre with distilled water in a 1 litre volumetric flask. Store in a polythene bottle.

(i) Intermediate Stock Solution for Ca. Mg, K and Na

To prepare an intermediate stock solution which contains 50 ppm Ca, 10ppm Mg, 10 ppm K and 5 ppm Na, take 5 ml of 1000 ppm Ca, 1 ml of 1000 ppm Mg, 1 ml of 1000 ppm K and 0.5 ml of 1000 ppm Na into 100 ml volumetric flask and fill to the mark with distilled water.

(ii) Working Standards for Ca, Mg, K and Na

Put 0, 2, 4, 6, 8 and 10 ml, of intermediate stock solution in 100 ml volumetric flask, add 2.0 ml Mehlich 3 Extractant and fill to the mark with strontium or lanthanum solution. The standards will contain 0, 1, 2, 3, 4 and 5 ppm Ca; 0. 0.2, 0.4, 0.6, 0.8, and 1.0 Mg; 0, 0.2, 0.4, 0.6, 0.8 and 1.0 ppm K and 0, 0.1, 0.2, 0.3, 0.4, and 0.5 ppm Na, respectively.

(b) Stock Solution for Fe, Cu, Mn and Zn

Iron: 1000 mg/L

Dissolve 1.000 g of iron powder or granules in 20 ml of 5 M hydrochloric acid and dilute to 1 litre with distilled water. Keep in a polythene bottle.

Copper: 1000mg/L

Dissolve 1 .000 g of copper metal in 50 ml of 5M nitric acid. Dilute to 1 litre in a volumetric flask with distilled water. Keep in a polythene bottle.

Manganese: 1000 mg/L

Dissolve 1.000 g of manganese metal in 50 ml of 5M hydrochloric acid. Dilute to 1 litre in a volumetric flask with distilled water. Keep in polythene bottle.

Zinc: 1000 mg/L

Dissolve 1.000g of zinc metal in 30 ml of 5M hydrochloric acid. Dilute to 1 litre in a volumetric flask with distilled water. Keep in a polythene bottle.

(i) Intermediate Stock Solution: Zn, Cu, Fe and Mn.

To prepare an intermediate stock solution of 400 ppm Mn, 400 ppm Fe, 8 ppm Zn and 4 ppm Cu, put 40 ml, 40 ml, 0.8 ml and 0.4 ml of 1000 ppm solutions of Mn, Fe, Zn and Cu respectively in 100 ml volumetric flask. Fill to the mark with distilled water.

(ii) Working Standards for Zn, Cu, Fe and Mn

Put 0, 2.5, 5.0, 7.5, and 10 ml of intermediate stock solution in 100ml volumetric flask and fill to the mark with Mehlich 3 Extractant and the standards will contain 0, 10, 20, 30 and 40 ppm Mn; 0, 10, 20, 30, and 40 ppm Fe; 0, 0.2, 0.4, 0.6 and 0.8 ppm Zn and 0, 0.1, 0.2, 0.3 and 0.4 ppm Cu respectively.

Determination of cations

Take 0.5 ml working standard extract and dilute to 25 ml with strontium or lanthanum solution and pass on AAS for calcium and magnesium and on flame photometer for potassium and sodium. Pass the extracts on AAS for Fe, Mn, Zn and Cu determination.

4.4.2 Detection of Phosphorous (Murphy-Riley method)

Reagents

Murphy Riley solution

(1) Dissolve 0.291 of antimony potassium tartrate in 100 ml distilled water.

(2) Dissolve 12g ammonium molybdate in 200 ml distilled water.

(3) In a 2 litre volumetric flask, add I litre water and then add140 ml concentrated sulphuric acid and add antimony potassium tartrate and ammonium molybdate solutions. Fill to the mark with distilled water and mix well.

Murphy- Riley Working Solution

Take 100 ml Murphy Riley solution, add 500ml water and 0.526 g ascorbic acid and mix well.

Standard phosphorus solutions

(1) Stock Solution for phosphorus

Dissolve 4.3940g of potassium dihydrogen orthophosphate (KH_2PO_4) in 250 ml of distilled water. Dilute to 1 litre in a volumetric flask. Keep in a polythene bottle. The solution will contain 1000 mg/l of P.

(2) Intermediate Stock Solution for phosphorus

Put 20ml of the above stock solution into 100ml volumetric flask and fill to the mark with distilled water. The solution will contain 200 mg/l of P.

(3) Working Standards for phosphorus

Take 0, 1, 2, 3, 4 and 5 ml of the intermediate stock solution into 100ml volumetric flask, add 10 ml Mehlich 3 Extractant, and fill to the mark with distilled water, and these will contain 0, 2, 4, 6, 8, and 10 ppm P.

Phosphorus determination on a ULTRA-VIOLET-Spectrophotometer

Take 1 ml aliquot of working standard or soil extract, add 9 ml Murphy Riley working solution and mix them. Pass at 882 nm after 15 minutes.

4.5 Determination of soil pH

The pH value of an aqueous solution is rigidly defined in terms of the concentration of H^+ and $0H^-$ ions in solution. The concept of "soil pH" is vague, but usually refers to the pH registered by a pH meter whose electrodes are immersed in a suspension of the soil in water or in suitable salt solution. However, the value obtained depends on the salt used, and on the soil: solution ratio, so that these experimental details must always be specified. Distilled water and a soil: solution ratio of 2:5 is normally used.

Apparatus

1. pH meter with universal glass electrode.
2. 4 oz extraction bottles

Reagents:

Buffer solutions at PH 4.0, 7.0 and 9.0, made up by dissolving the appropriate buffer tablets in water (I tablet per 100 ml: dissolve in a little hot water, allow solution to cool, then make up to volume).

Procedure:

1. Weigh out 20 g of soil into a 4 oz extraction bottle.
2. Add 50 ml distilled water. Screw on the lid and shake for I minute, 3 times, during the course of 30 minutes on a mechanical shaker.
3. Standardize the pH meter against the buffer solutions.
4. Shake the bottle a final time, remove the lid, and then lower the washed electrode into the suspension. Set the range switch to the "0-14 pH" position. Twist the bottle a little to ensure adequate mixing. Take the reading to the nearest 0.5 unit as soon as the reading is stable (about 30 to 60 seconds).

Switch back to the “7pH" position after taking the reading. Wash the electrode free from all solid particles, and then touch it gently with a piece of filter paper to remove the main drips. If large number of samples is being done, recheck against a buffer solution after every 10 to 15 samples. After use, leave the electrode immersed in 0.1N HCl. Avoid scratching, or even touching the electrode with anything other than the filter paper. Leave the instrument switched on always.

4.6 Soil particle size (mechanical) analysis (Bouyoucos or Hydrometer method)

Principle

The particle size analysis of a soil estimates the percentage sand, silt and clay contents of the soil and is often reported as percentage by weight of oven-dry and organic matter-free soil. The analyses are usually performed on air-dry soil. Based on the proportions of different particle sizes, a soil textural category may be assigned to the sample.

The first stage in a particle size analysis is the dispersion of the soil into the individual particles. These are the sand (2.00 - 0.05) mm), silt (0.05 - 0.002 mm) and clay (< 0.002 mm) fractions. Individual soil particles are often bound into aggregates hence the requirement for dispersion.

The hydrometer method of silt and clay measurement relies in the effects of particle size on the differential settling velocities within a water column. The settling velocity is also a function of liquid temperature, viscosity and specific gravity of the falling particle. Theoretically the particles are assumed to be spherical and to have a specific gravity of 2.65. If all other factors are constant then the settling velocity is proportional to the square of the radius of the particle (Stoke's law). In practice, therefore, we must know and make correction for the temperature of the liquid. Greater temperatures result in reduced viscosity due to liquid expansion and a more rapid descent of falling particles.

Reagents and apparatus:

1. Calgon (sodium hexametaphosphate) solution, 10%. Dissolve 100 gm of calgon in 1 litre of distilled water. This solution should not be kept over one month, when too old it losses its dispersing efficiency because it will be converted to another compound.
2. Amyl alcohol
3. Hydrometer with Bouyoucos scale in g/litre
4. Soil dispersing stirrer, a high speed electric stirrer with a cup receptacle.

Procedure:

1. Weigh out 50g of air-dry <2 mm soil (100g in case of very sandy soil) into a 400 ml beaker.
2. Saturate the soil with distilled water and add 10 ml of 10% Calgon solution. Allow to stand for 10 minutes.
3. Transfer the suspension to the dispersing cup and make to the mark in the cup with distilled water.
4. Mix the suspension for 2 minutes with an electric high speed stirrer. Use ordinary bottles if no cup is available. Shake the suspension overnight if no stirrer is available.
5. Transfer the suspension into a graduated cylinder (with a 1130ml mark) and rinse remaining soil into the cylinder with distilled water. Insert the hydrometer into the suspension and add water to 1130 ml, then remove the hydrometer.
6 Cover the cylinder with a tight-fitting rubber bung and mix the suspension by inverting the cylinder carefully ten (10) times. Note the time.
7 Quickly add 2 - 3 drops of amyl alcohol to the soil suspension in order to remove froth and after 20 seconds place the hydrometer gently into the column.
8 At 40 seconds, take a hydrometer reading and measure the temperature of the suspension.

9 Repeat step 6 (mixing of the soil suspension 10 times) and allow the cylinder to stand undisturbed for 2 hours.

10 After two hours, take both hydrometer and temperature readings.

11 Make the necessary temperature corrections (Table 38).

Table 38: Temperature correction for hydrometer reading of soil texture

Temperature (^{0}C)	Hydrometer correction (g/litre)
15	-2.0
16	-1.5
17	-1.0
18	-1.0
19	-0.5
20	0.0
21	+ 0.5
22	+1.0
23	+1.0
24	+1.5
25	+2.0

Temperature affects the hydrometer readings and, because the hydrometer has been calibrated at 68^{0}F (20^{0}C). Either correction factors must be applied or the determination should be conducted in a temperature controlled room, maintaining the 20^{0}C temperature.

Calculations:

% Sand

After 40 seconds, the sand has settled and the hydrometer reading reflects the grams of silt + clay in I litre of the suspension. To calculate the amount sand present in 1 litre of the suspension, subtract this value from the original sample weight. For example, if the hydrometer reading after 40 seconds corrected for temperature is 18.0 g/litre, then silt + clay weigh 18.0 g in the 1 litre soil suspension. Therefore, the sand weighs 50.0 – 18.0 = 32.0 g in the 1 litre suspension (of the original 50.0g air-dry soil sample). The percentage sand is

calculated by dividing the sand content (32 g) by the total (50 g) and multiplying by 100 as follows:

$$\% \text{ sand} = \frac{32 \times 100}{50} = 64\%$$

% Clay

After 2 hours, the silt has settled. The hydrometer reading now reflects the clay content of the original suspension. For example, if hydrometer reading after temperature correction is 4.7 g/litre, then the percentage of clay in soil is:

$$\% \text{ clay} = \frac{4.7 \times 100}{50} = 9.4\%$$

% Silt

The silt content is calculated by subtracting the sum of the clay and sand contents from 100% or:

%Silt = 100 - (9.4% clay + 64% sand) = 26.6%

Soil texture

Once the sand, silt and clay distribution is measured, the soil may be assigned to a textural class based on the particle size distribution using the soil textural triangle (Figure 23).

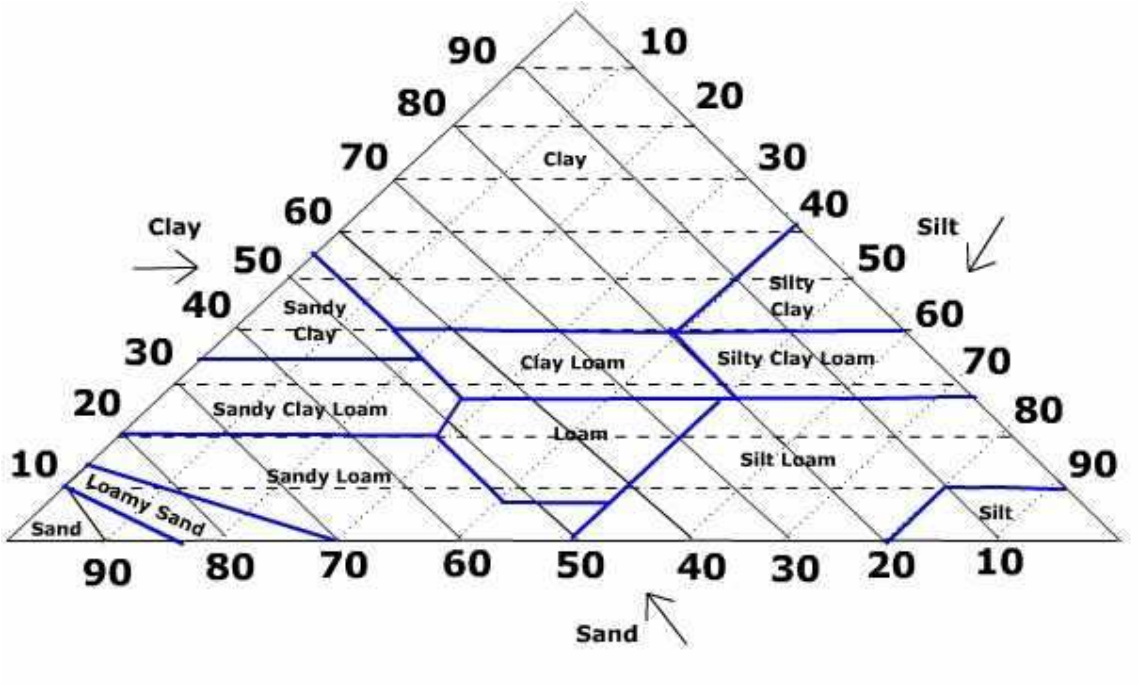

Figure 23: Soil Textural Triangle

Within the textural ‘triangle’ are various soil textures which depend on the relative proportions of soil particles. Users simply obtain the appropriate texture on the particle size distribution. In the example above (64%'sand, '27% silt and 9% clay), the corresponding soil texture is a sandy loam.

Procedural notes:

1 Cylinders for particle size analysis are calibrated depending upon the volume of the hydrometer in use. At NARC Muguga, the calibration is 1130 ml, indicating the final volume of the soil suspension with the hydrometer inserted.

2. Many laboratories have developed their own temperature conversion tables depending on the exact procedure and working conditions.

4.7 Water holding capacity

Field capacity is defined as the maximum amount of water the freely drained soil can hold and is estimated after a saturated soil has been allowed to drain without allowing its moisture stores to be depleted by evaporation. The method is as follows:

1. Build an earth bund around a 1 m x 1 m area, and fill with water.
2. Refill with water as necessary so that approximately 50 cm^3 of water has soaked into the soil.
3. Cover the area with a plastic sheet in order to prevent evaporation and leave for 2 days.
4. Bulk 4 replicated 0- 10 cm soil samples from near the centre of the area.
5. Put about 250 g of the wet soil in a moisture can of known weight (W_I), weigh (W_2), dry the soil at 105^0C for 48 hours and cool.
6. Weigh the cooled dry soil with the moisture can (W_3).

Calculation:

% soil moisture at field capacity = $$\frac{(W_2 - W_3)\times 100}{(W_3 - W_1)}$$

The Lower Limit of Plant Available Water

This value is sometimes known as wilting point and is often equated to the soil water content at 15 bar (or 1.5 Mpa) water potential. This value is obtained as follows:

1. Distribute rubber sample rings or metal rings with cheesecloth fastened to one end with a rubber band around a pre-soaked 15 bar ceramic plate. Weigh container (W_1)

2. Fill each ring with soil. Do not compress or pack the soil into the ring. Prepare triplicate samples.

3. Place the plate in a large tray and slowly add tap water until the water is about half way to the top of the sample rings. Soak the samples overnight.

4. Seal the outflow tube on the ceramic plate with a clamp. Carefully drain excess fluid out of the tray. A syringe or siphon works well.

5. Place the plate (with sample) in the pressure chamber. Connect the outflow tube of the ceramic plate to the fitting on the inside of the chamber. Connect another tube to the fitting on the outside of the chamber, and place the free end of the tube in a beaker of water. Unclamp the outflow tube so that water may flow freely from the ceramic plate to the beaker on the outside of the chamber.

6. Place a damp cloth over the samples in the chamber to maintain high humidity while the samples are equilibrating. Close the chamber, tighten the ring nuts, and slowly apply air pressure to the chamber until 15 bars is reached.

7. Allow the samples to equilibrate for 2 to 4 days. The longer time is for soils with high clay contents.

8. Before releasing air pressure, clamp the outflow tube so that water may not re-enter the ceramic plate.

9. Release pressure slowly. Open the chamber and remove the samples and weigh them (W_2).

10. Dry the soils at 105^0C for 48 hours, cool and weigh (W_3).

Calculation

The lower limit of plant available water (%) = $\frac{(W_2 - W_3)}{(W_3 - W_1) \times 100}$

where WI = weight of container (g), W2 = weight of container + wet soil (g) and W3 = weight of container + oven dry soil

Plant Available Water Capacity (PAWC)

The amount of water which a given soil horizon can store for plant use is estimated from the difference between the field capacity and lower limit of plant available water for the horizon. It is expressed as an equivalent depth of water (mm), and is calculated as follows:

PAWC = (field capacity –lower limit) × Dsoil × Z, where Dsoil is the bulk density of the horizon and Z is the thickness of the horizon in mm.

The total PAWC is the sum of the PAWC of all horizons down to effective rooting depth.

5 Example of chromatogram from liquid chromatograph