FATE AND TRANSPORT OF AGRICULTURAL HERBICIDES AND VETERINARY ANTIBIOTICS IN THE PRESENCE OF A NON-IONIC SURFACTANT

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ABSTRACT

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Doctor of Philosophy **Bioresource Engineering**

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Many parts of the world, and especially developing countries, are experiencing severe water shortage problems. This is causing increased use of untreated or partially-treated wastewater for irrigation. Consequently, many pollutants such as surfactants, present in wastewaters, could influence fate and transport of agricultural chemicals in soils. Therefore, a field lysimeter study was undertaken to investigate the effect of non-ionic surfactant, Brij 35, on the fate and transport of two commonly used antibiotics, oxytetracycline (OTC) and monensin (MON), and an herbicide, metribuzin. Twenty seven PVC lysimeters, 1.0 m long x 0.45 m diameter, were packed with a sandy soil to a bulk density of 1.35 Mg m^{-3}. Cattle manure, containing these compounds, was applied at the surface of the lysimeters at the recommended rate of 10 t/ha. Three types of wastewaters, i.e., good, poor, and very poor, were simulated by using three aqueous Brij 35 concentrations of 0, 0.5 and 5.0 g L^{-1}, respectively, and applied to lysimeters, in triplicate, for each compound. Over a 90-day period, soil and leachate samples were collected and analyzed. Sorption experiments were also conducted for all compounds in the laboratory in the presence and absence of surfactant.

Overall, the OTC and monensin mobility in the lysimeter study significantly increased in the presence of the surfactant ($p<0.01$). The maximum OTC concentration in the leachate was 102.72 µg L^{-1} for the surfactant concentration of 0.5 g L^{-1}, which was higher than both control and the high surfactant concentration treatment. Unlike OTC, monensin leaching increased significantly with increasing surfactant concentration ($p<0.01$), and the maximum detected concentration in the leachate was 5.83 μg L^{-1} for the surfactant concentration of 5.0 g L^{-1}.

The laboratory study also showed that the sorption coefficient of OTC significantly reduced in the presence of the surfactant ($p<0.05$); it changed from 23.55 mL g^{-1} in the aqueous medium to 19.49, 12.49 and 14.53 mL g^{-1}, respectively, in the presence of the surfactant at concentrations of 0.25, 2.5 and 5 g L^{-1}. It may, however, be noted that the sorption coefficient was higher for the highest surfactant concentration used. However, in the case of monensin, the sorption coefficient reduced significantly ($p<0.01$) from 120.22 mL g^{-1} in the aqueous medium to 112.20, 100 and 63.09 mL g^{-1} with surfactant concentrations of 0.25, 2.5 and 5 g L^{-1}, respectively.

Herbicide movement may also be affected by surfactants; therefore, the mobility of a commonly-used herbicide, metribuzin, was investigated. In the presence of the surfactant, a significant increase in metribuzin movement ($p<0.05$) in the soil profile was observed. The highest metribuzin concentration in the leachate was 84.80 μg L^{-1} for the 5.0 g L^{-1} surfactant treatment. However, no significant differences on mobility were observed for the two treatments with differing surfactant concentrations. The laboratory sorption study showed that the sorption coefficient of metribuzin significantly decreased with increasing surfactant concentration ($p<0.05$).

It can be concluded that nonionic surfactants may increase the mobility of agricultural pollutants, including antibiotics and herbicides, in soil. Therefore, irrigation with poor quality water can potentially cause ground water contamination.

Résumé

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Plusieurs régions du monde, particulièrement celles en voie de développement, souffrent d'une pénurie d'eau. Afin de composer avec l'augmentation de la demande en produits alimentaires et la pauvreté au sein d'une population croissante, des eaux usées partiellement- ou non-traitées servent souvent a l'irrigation. Il en survient que plusieurs polluants, incluant des agents de surface, peuvent être présents dans ces eaux d'irrigation et influencer le devenir et le transport de pesticides et antibiotiques dans les sols agricoles. Une étude lysimétrique au champ visa à évaluer l'effet de l'agent de surface non-ionique, Brij 35, sur le devenir et le transport de deux antibiotiques, l'oxytétracycline (OTC) et le monensin (MON), ainsi qu'un herbicide le metribuzin. Vingt-sept lysimètres en PVC, hauteur 1.0 m × diamètre intérieur 0.45 m, furent remplis d'un sol sablonneux à une densité apparente de 1.35 Mg m^{-3}. Du fumier de vache, contenant les composés sous étude fut épandu à la surface des lysimètres au taux recommandé de 10 Mg ha^{-1}. Pour chaque polluant, chacun des trois lysimètres répliquats fut arrosé d'une des trios solutions aqueuses de l'agent de surface Brij 35 (0, 0.5 ou 5 g L^{-1}), représentant une qualité d'eau d'irrigation 'bonne,' 'mauvaise' ou 'très mauvaise'. Sur une durée de 90 jours, des échantillons de sol et de lixiviat furent obtenus et analysés. Des expériences en laboratoire additionnelles furent conduites en réacteur pour évaluer le potentiel de sorption des composés à l'étude.

La présence de l'agent de surface non-ionique Brij 35 diminua de façon significative ($p<0.05$) le coefficient de sorption de l'OTC, soit de 23.55 ml g^{-1} en milieu aqueux, à 19.49, 12.49 et 14.53, respectivement, en la présence de 0.25, 2.5 et 5 g L^{-1} de Brij 35. La mobilité de l'OTC fut significativement moindre en présence de 0.5 g L^{-1} *vs.* 5.0 g L^{-1} de Brij 35. La concentration maximale en OTC du lixiviat fut de 102.72 µg L^{-1}. Le coefficient de sorption du MON diminua de

façon significative ($p<0.05$) de 120.22 mL g^{-1} en milieu aqueux, à 112.20, 100 et 63.09 mL g^{-1}, respectivement, en présences de 0.25, 2.5 et 5 g L^{-1} de Brij 35. Si la demi-vie ($t_{½}$) du MON fut de 5.72 jours en eau du robinet, elle augmenta à 9.62 et 11 jours, respectivement, en presence de 0.5 et 5.0 g L^{-1} Brij 35. La concentration maximale de MON détecté dans le lixiviat fut de 5.83 µg L^{-1}.

Dans le laboratoire, la sorption/désorption de l'OTC fut comparé à celle du sulfachloropyidazine (SCP) en présence et en absence d'un agent de surface non-ionique. En contraste à l'OTC, la présence d'un agent de surface augmenta de façon significative le potential de sorption du SCP au sol, tel qu'en témoigne le coefficient de sorption coefficient (K_F) pour le SCP qui augmenta de 19.95 mL g^{-1} en absence de Brij 35, à 95.49 mL g^{-1} et 66.06 mL g^{-1} en présence de Brij 35 à des concentrations de 2.5 g L^{-1} et 5 g L^{-1}, respectivement. Le coefficient de désorption de l'OTC en l'absence d'agent de surface fut de 61.58 mL g^{-1}, tandis qu'en présence de 2.5 g L^{-1} Brij 35 elle diminua à 50.35 mL g^{-1}. Comparativement, pour le SCP, les valeurs correspondantes furent de 1.24 and 1.38 mL g^{-1}. Un phénomène d'hystérèse dans le cas du SCP en présence *vs.* absence de Brij 35 indiqua le bas potentiel de lixiviation du SCP en présence d'un agent de surface. Cependant, l'OTC se montra facilement désorbée en présence de Brij 35 en forme micellaire.

Vu les inquiétudes quant a l'utilisation constante d'herbicides dans la production agricole actuelle, le potentiel d'une mobilité accrue de l'herbicide métribuzine en présence d'agents de surface s'avéra digne d'attention. La métribuzine présenta une mobilité accrue et une moindre affinité de sorption au sol et $t_{½}$ en présence de micelles de Brij35 comparé à en leur absence. Les agents de surface ont augmenté la mobilité en sol des polluants étudiés. L'irrigation avec des eaux de mauvaise qualité peut donc poser un risque de contamination des eaux souterraines.

Preface and contribution of Authors

The chapters of this thesis have been presented at scientific conferences and submitted for publication to peer reviewed journals. The author of this thesis was responsible for establishing, maintaining and introducing various modifications in the field setup of the study and carrying out other research and analytical work in both field and laboratory. She was also responsible for the preparation of all manuscripts and presentations enlisted under this topic. Dr. Shiv Prasher is the thesis supervisor. He was actively involved in all stages of the study, providing scientific advice and technical supervision at every step of the project. He was also directly associated with editing and reviewing the prepared manuscripts.

Dr. Ramanbhai Patel is a Research Associate who has worked on various Departmental research ventures. He was constantly engaged in various aspects of the project, particularly in field related work and he co-authored one of manuscripts.

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Table of Contents

List of Tables

List of Figures

List of Abbreviations

AEs	Alcohol ethoxylates
APEOs	Alkylphenol ethoxylates
BOD	Biochemical oxygen demand
CAFO	Concentrated animal feeding operation
CMC	Critical micelles concentration
DAD	Diode array detector
DOM	Dissolved organic matter
ECs	Emerging contaminants
ELISA	Enzyme link immune assay
EMEA	European Agency for the Evaluation of Medicinal products
HLB	Hydrophilic-Lipophilic balance
HLPC	High Performance Liquid Chromatography
HOCs	Hydrophobic organic compounds
K_d	Distribution coefficient
K_F	Freundlich coefficient
K_L	Langmuir coefficient
K_{oc}	Organic carbon coefficient
K_{ow}	Octonal water coefficient
OC	Organic carbon
OTC	Oxytetracycline
MON	Monensin
MSR	Molar solubilization ratio
MTR	Metribuzin
NP	Nonylephenol
PEG	Polyethylene glycol
PhACs	Pharmaceutically active compounds
PNEC	Predicted no effect concentration

R^2	Determination coefficient
SCP	Sulfachloropyridazine
SOLAW	State of the World’s Land and Water Resources for Food and Agriculture
$t_{½}$	Half-life
TII	Thermodynamic index of irreversibility
USEPA	United States Environment Protection Agency
WWTP	Waste water treatment plant
ZPC	Zero point of charge

Chapter 1 - General Introduction

In many parts of the world, water scarcity is an increasing problem. Globally, water resources are limited and getting more stressed due to population growth, industrialization, climate change and shifting consumption patterns. Since agricultural activities utilize 63% of the total freshwater (Bakkes et al., 2008), effective strategies are needed to bridge the supply/demand gap in water resources. Using wastewater for agriculture is becoming an important management option, particularly in arid regions. Drechsel et al. (2010) reported that 46 countries, representing 75% of the world's irrigated land, use wastewater for irrigation. Worldwide, Hamilton et al. (2007) estimated that approximately 20 million hectares of land are irrigated with wastewater; this is expected to see a marked increase in the next few years. Chatterjee (2008) also indicated that 85% of 53 cities in developing countries discharge untreated or primary treated, wastewater into rivers.

Use of wastewater for irrigation appears to be a good option, especially considering the increasing demands for fresh water in the society. Generally, the chemical composition of wastewater is a function of the various products used by individual households combined with the input of industrial effluents. Many chemicals found in these effluents could provide an input pathway for several contaminants to soil via the application of wastewater irrigation. This could cause a buildup of contaminants in the soil and may lead to their uptake by plants. From there, they could reach the human food chain.

1.1 Background

1.1.1 Surfactants in the environment

Surfactants have been detected as the highest concentrations among organic chemicals in wastewater and sludge (Brunner et al., 1988; Field et al., 1992; Wild et al., 1990). In industrial wastewater, the concentration of surfactants may range from 10^2-10^3 mg L^{-1} (Narkis and Ben-David, 1985). The application of such wastewater onto the land introduces a large amount of surfactants into the soil (Hutchins et al., 1985; Amiel et al., 1990).

The growing increase of household products is resulting in the abundance of surfactants in urban sewers (Conn et al., 2006; Loyo-Rosales et al., 2007; Stuart et al., 2012). Wastewater treatment plants (WWTP) can remove surfactants but they may not remove all their metabolites, such as nonylphenol ethoxylates (NPEOs) (Loyo-Rosales et al., 2007). The presence of surfactants in the environment has major biological implications. Non-ionic surfactant by-products are estrogen disrupting compounds. They mimic natural sex hormones and this may result in changes in the sex ratio, malformations and even result in a decrease in the fish populations (Esperanza et al., 2004). More importantly, surfactants have been detected in ground water and drinking water supplies (Reemtsma and Jekel, 2006). Surfactant degradation products, nonylephenols (NPs), have also been found in potable water in the US (Barber et al., 2009). Safer nonionic surfactants, such as alcohol ethoxylates (AEs), are increasingly used but their environmental impact on agricultural activities is not fully understood.

The presence of nonionic surfactants in irrigation water may adversely affect the transport of organic compounds in soil (Huggenberger et al., 1973; Kan and Tomson, 1990; Aronstein et al., 1991; Rodriguez-Cruz et al., 2004). Generally, non-ionic surfactants increase the downward movement of pesticides in soil whereas cationic surfactants decrease the mobility of pesticides in soil. Katagi (2008), however, reported that the mobility of pesticides is increased in leached water when there are high concentrations of nonionic surfactants. However, Tao et al. (2006) indicated that, even at low concentrations (0-20 mg L^{-1}), these surfactants have the potential to decrease sorption and mobilize herbicides.

1.1.2 Pharmaceutical antibiotics

Over the last decade, the presence of pharmaceutical antibiotics in the environment has become a concern. As one of the emerging contaminants (ECs), antibiotics are introduced into the environment by several pathways; these include medical waste, discharge from wastewater treatment facilities, leakage from septic systems and agricultural waste storage structures, overland flow, landfill with human and agricultural wastes and transport from agricultural lands receiving manure and slurry from intensive livestock operations (Halling-sorenson et al., 1998; Kay et al., 2005; Michael et al., 2013). In US, Carlson (2004) conducted a survey in a network of 139 streams across 30 states during 1999 and 2000; they reported that 14 out of 24 antibiotics were found in 80% of the streams sampled. The measured concentrations in water samples were as high as 1.9 $\mu g\ L^{-1}$.

Generally, veterinary antibiotics account for about half of all antibiotics used in the United States (Qiang et al., 2006). In particular, in the US and Canada, the reported amount of antibiotics used in the livestock industry was about 16 million kg annually, of which approximately 70% were used for non-therapeutic purposes (UCS, 2001). However, in the EU, 5 million kg of antibiotics were used; of this amount, 3.5 and 1.5 million kg were used for therapeutic purposes and as growth promotion, respectively (Kay and Boxall, 2000; Alder et al., 2000). From the extensive use of antibiotics, compounds such as tetracyclines, sulfanomides (sulfachlorpyridazine) and ionophores (monensin) are continuously being released into the environment from anthropogenic sources such as wastewater treatment plants as well as runoff from agricultural fields (Jones et al., 2001; Heberer, 2002; Miao et al., 2004; Batt et al., 2007; Gulkowska et al., 2008; Kummerer, 2009). Concentrations up to 5 $\mu g\ L^{-1}$ have been detected in sewage treatment plant (STP) effluents in Germany. More importantly, antibiotics are poorly metabolized in the animal gut, resulting in as much as 90% of the antibiotics excreted in the parent form or as metabolites (Halling-sorensin, 1998). These metabolites can also be bioactive, and can be transformed back to the parent compound after excretion (Langhammer, 1989). Thus, a substantial percentage of the administered antibiotics are expected to be released back into the environment in an active form (Warman and Thomas, 1981; Berger et al., 1986).

The habitual presence of antibiotics in environmentally relevant concentrations has been associated with the development of microbial resistance (Schwartz et al., 2006; Kummerer, 2009); there is the increasing likelihood that the therapeutic effect of these antibiotics against human and animal pathogens will be limited (Kemper, 2008). This is worrying since aquatic bacteria are regularly exposed to antibiotics (Rosal et al., 2010). The possibility of the transfer of antibacterial resistance from agriculture to humans has been reported (Rhodes et al., 2000, Bogaard et al., 2000; Sengelov, 2003 and Gullberg et al., 2012). Although point source of pollution is well identified and can be controlled, a comprehensive approach is needed to assess the impact of the effect of veterinary antibiotics on soil biota and groundwater contamination in agricultural areas.

1.1.3 Pesticides

Agricultural effluents are a known major non-point source for pesticide pollution. Pesticides can potentially enter surface water by several routes such as disposal sites and landfills, where industrial and agricultural wastes are buried without treatment, as well as discharges from industrial effluents from pesticide production plants. Furthermore, spray drift, surface runoff, and field drainage are relevant routes; therefore, contamination via groundwater discharge is a likely possibility. Due to the fact that many pesticides are either partially or completely resistant to breakdown during the wastewater treatment processes, these compounds easily enter the aquatic environment.

In the U.S., about 2.2 billion kilograms of pesticides are used annually, with agricultural usage accounting for 77% (Kiely et al., 2004); herbicides are the most common in this group. They account for 65% of the total amount applied. It is not surprising that some herbicide residues have been detected in the atmosphere. For example, atrazine and alachlor have been detected in rainwater at concentrations exceeding the allowable level in drinking water in the US (USGS, 1995). Moreover, about 46 different pesticides have been detected in ground water and 76 pesticides in surface water bodies (USEPA, 1998).

The fate and transport of pesticides is governed by sorption, leaching and degradation. Each process depends on the physicochemical structure of the pesticide as well as soil type and bioavailability. It is estimated that only 0.1% of the total amount of pesticide applied actually reaches the target. Consequently, a significant amount is expected to be released into the environment. Furthermore, evidence of the deleterious effects on non-target organisms has been reported (Pimentel and Levitan, 1986). Therefore, it is essential to investigate the mobility of herbicides in order to evaluate the ramifications of their presence in the soil-water systems.

1.2 The Project

From the above mentioned discussion, it can be seen that use of wastewater is of great importance in coping with the long term imbalances resulting from water demand and the lack of water resources. However, this wastewater contains a number of contaminants such as surfactants, antibiotics and herbicides. The application of manure as a soil amendment is also a common practice, which introduces antibiotics into the soil. Surfactants could affect the movement of antibiotics in soil resulting in the contamination of water bodies. The situation is similar with herbicides. Since they are applied regularly to soils to control weeds, their leaching potential could change in the presence of surfactants. Therefore, investigation of the fate and transport of chemicals when they coexist with other contaminants in wastewater is necessary. These factors must be understood in order to integrate water quality in wastewater use and to implement a strategy by which wastewater use becomes an environmentally friendly option.

1.3 Research Objectives

Surfactants can affect the persistence and mobility of antibiotics and pesticides in soil and water. The impact of different concentrations of nonionic surfactants in semi-treated and untreated wastewater could have a varying effect on the mobility of chemical contaminants in soil. Therefore this research was planned with the following objectives:

- To study the effect of the presence of a non-ionic surfactant in irrigation wastewater on the fate and transport in soils of two commonly-used antibiotics, namely oxytetracycline and monensin;

- To investigate the fate and transport of herbicide metribuzin in soil in the presence of a nonionic surfactant in irrigation wastewater;

- To determine the sorption isotherms for the two antibiotics and the herbicide in the absence/presence of a non-ionic surfactant; and

- To assess the effect of the surfactant concentration on the desorption efficiency of immobile and mobile antibiotics, i.e. oxytetracycline and sulfachloropyridazine, in soil.

1.4 Thesis organization

The thesis contains nine chapters.

Chapter 1: Provides an introduction to the research topic, followed by a listing of the objectives and scope of this investigation.

Chapter 2: Documented support and perspective to subsequent chapters, a review of relevant and applicable literature, along with a historical background of the subject, are provided.

Chapter 3: Effect of non-ionic surfactant Brij 35 on the fate and transport of oxytetracycline antibiotic in soil

Chapter 4: Fate and transport of monensin in the presence of non-ionic surfactant Brij 35 in sandy soil

Chapter 5: Sorption / desorption behavior of oxytetracycline and sulphachloropyridizine in the Soil Water Surfactant System

Chapter 6: Effect of the Presence of Nonionic Surfactant Brij 35 on the Mobility of metribuzin in soil

Chapter 7: General summary and conclusion

Chapter 8: Contributions to knowledge and suggestions for further research

Chapter 9: References

Chapter 2 – Literature Review

2.1 Reuse of wastewater

Water is a very complex and dynamic resource. It occurs in a very dynamic cycle of rain, runoff and evaporation, with enormous spatial-temporal and quality variations that significantly impact people and ecosystems (Rijsberman, 2006). In the past, the global water resources were perceived as cheap and unlimited, however it is now realized that it is scarce, finite and valuable. Although there is 140 billion km^3 of water available on the planet, only 3 % is fresh water. Further, 97% of the fresh water is stored in ice caps and glaciers, while 2% and 1% are in ground water and easily accessible surface water, respectively. The 1% easily available water can be found in soil moisture (38%), lakes (52%) and the remaining 10% in rivers, atmosphere and in living organisms (World Meteorological Organization, 1997). Expanding populations and the associated growth in industrial and agricultural water demands have led to increased competition over limited water resources. Local and national demands for limited resources result in heightened competition among the many users. The 1997 United Nations assessment of fresh water resources indicated that one third of the world's population live in countries experiencing moderate to high water stress. Moderate to high stress translates to consumption levels that exceed 20% of available supply (World Meteorological Organization, 1997).

There is no commonly accepted definition of water scarcity, however, a number of indicators and indices have been utilized as measures of water well-being (Gleick, 2002; Rijsberman, 2006). The Falkenmark indicator or ‘‘water stress index’’ is most widely used. This index establishes the threshold of 1700 m^3 of renewable water resources per capita per year, based on estimates of water requirements in the household, agricultural, industrial and energy sectors, and the needs of the environment. When supply falls below 1000 m^3 and 500 m^3 a country experiences water scarcity and absolute scarcity, respectively (Falkenmark et al., 1989). A modification of the water stressed index, which accounts for a society's adaptive capacity has been proposed by Ohlsson (Ohlsson, 1999; 1998) and is called ‘‘Social Water Stress Index’’. Other indices include, the water resources vulnerability index (Raskin et al., 1997; Shiklomanov, 1991), the physical and economic scarcity indicators (Seckler et al., 1998), and Water Poverty Index (Sullivan et al., 2003). All global water scarcity models have concluded that a large share of the world population will be affected by water scarcity over the next several decades (Raskin et al., 1997; Seckler et al., 1998; Shiklomanov, 1991; Vorosmarty et al., 2000; Wallace & Gregory, 2002). Many countries in the arid areas of the world, particularly Central and West Asia and North Africa, are already close to, or below the 1000 m^3/capita/year threshold (Rijsberman, 2006). Wallace (2000) estimates that all of North, Eastern and Southern Africa, and the Middle East, will drop below 1000 m^3/capita/year before 2050. West Africa and large parts of South and Southeast Asia would be in the 1000 to 2000 ranges at that time. In the absence of environmental considerations, various analyses have indicated that there is no water scarcity in the developed world (Europe, North America, Australia, and Japan).

Recent updates by The State of the World’s Land and Water Resources for Food and Agriculture (SOLAW) estimates that by 2050, rising populations and incomes will require a 70% increase in global food production. In quantitative terms this will be equivalent to another one billion tons of cereals and 200 million tons of livestock products produced annually (FAO, 2011). Presently agriculture accounts for over 70% of the world's water withdrawal (Raskin et al., 1997). 40% of global crop production comes from the 18% of irrigated agricultural lands and employs about 30% of the global population in rural areas. In contrast, rain-fed agriculture accounts for 80% arable lands and produces 60% of the world’s food (De Wrachien, 2003; Rockstrom & Falkenmark, 2000). In the developing world, approximately 20 percent of arable land is irrigated; however the prevalence of irrigation varies widely within and among countries and crops. Irrigation makes the most significant contribution to global food security in Asia, representing nearly two-thirds of the total global irrigated area. These lands account for as much as 80, 70 and 50% of food production in Pakistan, China and India and Indonesia, respectively (Barker & Molle, 2004). In Spain, irrigated agriculture represent 60% of agricultural production, utilizing 19% of the cultivated area (3.6 million hectares) and consumes 80% of the total water supply (Berbel & Gómez-Limón, 2000).

In order to overcome the water deficits and cope with the ever increasing food demand, about eighty eight developing countries decided to use wastewater for irrigation as a common practice (e.g. across Asia, Africa, Latin America, etc.). Eventually, wastewater became the only source of water for irrigation in these areas, even in areas where clean water sources exists; small farmers prefer to use wastewater as an alternative of expensive chemical fertilizers because of its high nutrient content (Namara et al., 2003). The impacts (natural and anthropogenic) are essentially unpredictable on a local scale, and therefore, water resources management should be flexible so as to be able to cope with changes in availability and demands for water. Bouwer (2000) further added that this would necessitate a holistic and integrated water management approach, where all pertinent factors are considered in the decision making process.

Fundamentally**,** the natural and anthropogenic impacts are unpredictable on a local scale, and therefore, standards for wastewater reuse for irrigation in many countries have been controlled by the guidelines of USEPA (1992) and the Environment ACT (1999) .

2.2. Surfactants

Surfactants are the major components of detergents found in domestic wastewater; this is due to their wide use in many industrial, commercial and household products such as detergents, emulsifiers, wetting and dispersing agents in pesticides formulations, antistatic agents and solubilizers.

Globally, the surfactant market is expected to produce revenues of more than US$41 billion by 2018, which is equal to an average annual growth of 4.5% with roughly a 37% share of global consumption. Asia-Pacific is the largest producer of surfactants, followed by North America and Western Europe. Furthermore, worldwide demand for anionic surfactants was approximately 6.5 million tons in 2010. It is estimated that the global combined demand for anionic and non-ionic surfactants is approximately 85%. The production of non-ionic surfactants is expected to exhibit the strongest growth between 2010 and 2018. Despite the global change to use non-ionic surfactants over the anionic surfactants, the latter continues to be the second-largest product group, especially in Africa, the Middle East, and Asian countries, with the exception of Japan and South Korea (Ceresana, 2012). Due to its prevalence, surfactants are common constituents in municipal effluents and in the corresponding receiving fresh-water and saltwater environments.

Due to the accumulation of surfactant molecules in aqueous solution gathering on different interfaces (such as, liquid/liquid; liquid/air or solid/liquid interfaces), the distance between the water molecules increases. As a result, a reduction in surface tension is more likely to occur. Being amphiphilic compounds, surfactants have a hydrophilic head and a hydrophobic tail.

To better understand the hydrophobicity and the hydrophilicity characteristics of a surfactant, a hydrophilic–lipophilic balance (HLB) has been established (Griffin, 1949) in equation 2.1, where M_h and M are the molecular masses of a hydrophilic moiety and the whole molecule, respectively.

$$HLB = 20 * (M_h M^{-1}) \qquad \text{Eq2.1}$$

Consistently lower values indicate that a surfactant is hydrophobic and the higher values indicate that the molecule is hydrophilic. At lower concentrations, surfactant molecules are dissolved in water as monomers. However, they have unique features; once they reach the point of critical micelles concentration (CMC), they tend to aggregate and form spherical shapes, called micelles (Bunton et al., 1991; Ying, 2006). These micelles are active colloidal aggregates and optically transparent but scatter light. Furthermore, depending on the concentration of surfactants and the solution composition, the size and shape could vary. Generally, the HLB scale ranges from 0-20; specifically, surfactants, which have HLB values from 10-20 are commonly used for industrial applications (Diallo et al., 1994). Typically, the CMC values of nonionic and zwitterionic surfactants are much lower than their corresponding ionic surfactants of the same alkyl chain length. As a general rule, the longer a hydrophobic alkyl chain, the lower the CMC value. Besides increasing the length of the hydrophilic group, poly (ethylene oxide) in the nonionic surfactants results in an observed elevation of the CMC level.

One of the recognized features of surfactants is the ability to increase the apparent water solubility of chemical compounds. It is stated that the extent of their ability is governed by factors such as their polarity and the size of the solubilized chemical and the surfactant properties such as CMC value, aggregation number, and shape of micelle (Fig 2.1). Basically, the apparent water solubility increases in proportion to the concentration of coexisting surfactants at the CMC level and markedly above CMC.

As an indicator for such solubilizing of chemicals by surfactants, the molar solubilization ratio (MSR), is used. It also can be denoted as the slope above CMC.

MSR is defined as follows (Eq 2.2):

$$\mathrm{MSR} = (S_{mic} - S_{cmc}) / (C_s - cmc) \qquad \text{Eq. 2.2}$$

where C_s, S_{mic} , and S_{cmc} are concentration of surfactant (mol L^{-1}), and apparent solubilities of substrate (mol L^{-1}) at $C_s > cmc$ and $C_s = cmc$, respectively (Edwards et al., 1991).

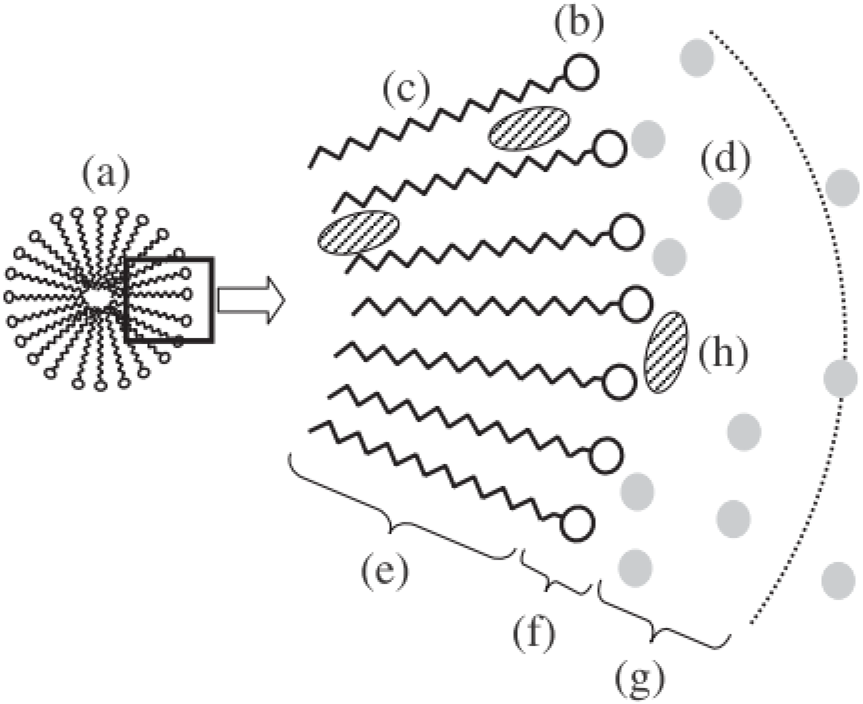


Figure 2.1 Schematic representation of spherical micelle: (a) spherical micelle, (b) polar head group of a surfactant, (c) hydrophobic moiety of a surfactant, (d) counterion, (e) hydrophobic core region,(f) Stern layer, (g) Gouy–Chapman double layer, (h) substrate molecule solubilized in micelle (Katagi, 2008).

2.2.1 Surfactant occurrence

Being a point source of contamination, WWTP effluents may contribute to the presence of many emerging contaminants (ECs) in the environment. Generally, the chemical composition of municipal wastewater is a function of the chemicals consumed by individual households and the contribution of industrial effluents. Depending on the performance and the efficiency of WWTPs in removing ECs, the occurrence of these chemicals will vary. Due to a lack of good functioning WWTPs in many developing countries, waste water is used partially treated or untreated for irrigation for agricultural purposes. Collectively, the land application of wastewater and sludge has become an important input entry for surfactants. Therefore, irrigation with poor quality waste water combined with land applications of sludge can load the soil water system with tremendous amounts of chemicals and as a consequence, increases the amount of dissolved organic matter (DOM) in the infiltration water. This enhances the mobility of these contaminants in reaching ground water (Kulshrestha et al., 2004). Further, factors such as the type, chemical, physical and hydraulic properties of soil and the characteristics of the solute are of importance in evaluating the transport of chemicals in the presence of DOM (Hutchins et al., 1985).

Due to their extensive use in many applications, surfactants are one of the ECs frequently detected in wastewater and sludge (Brunner et al., 1988; Field et al., 1992; Wild et al., 1990). These compounds are amphiphilic molecules containing the polar group represented by an ethylene oxide head and a non-polar tail represented by a long alkyl chain. In the United States, about 7 million tons of biosolids are produced annually in WWTPs resulting in a potential release of several million kilograms of surfactants into soil after the application of wastewater (Xia, 2001). Therefore, the consistent application of waste water may increase the amount of less biodegradable surfactants in the soil-water system (Abu-Zreig, 2003).

During waste water treatment, the hydrophilic heads are shortened and transformed to monoethoxylate (NP1EO) and diethoxylate (NP2EO). These compounds are totally deethoxylated to nonylphenols (NPs), which are more hydrophobic, toxic and more persistent. More importantly, they become estrogenic to aquatic organisms at relatively low concentrations. WWTPs do not eliminate all these metabolites efficiently (Loyo-Rosales et al., 2007). Consequently, NPs were detected at high concentrations ranging from 1.8 to 25 g L^{-1} in two rivers in Switzerland (Ahel et al., 1996). Also, NPs were detected at concentrations up to 2 g kg^{-1} in sludge from a WWTP receiving industrial wastewater (Minamiyama et al., 2006). In Kansas, concentrations up to 898 mg kg^{-1} of NPs have been measured in biosolides from WWTPs (Keller et al., 2003). In the US, concentrations from 9.4-309 g L^{-1} of NPs were detected in leachate (La Guardia et al., 2001). Interestingly, the presence of NPs in water can induce water-air volatilization and high concentrations have been measured in the atmosphere in New York. Concentrations up to the of 56.3 ng m^{-3} were detected at coastal areas and 81 ng m^{-3} at a suburban site. This suggests that the presence of NPs in the atmosphere can negatively affect human health and pose a risk on the ecosystems receiving treated sewage effluents (Van Ry et al., 2000). NPs have a half-life of more than 60 years (Soares et al., 2008).

Petrovic et al. (2008) reported that concentrations of nonylphenol ethoxylates (NPEOs) in WWTP influents vary from less than 30 to 1035 μg L^{-1}. However, concentrations up to 22500 μg L^{-1} have been detected in industrial wastewater. In addition, the concentration of NP, as the most toxic and most potent estrogen disruptor compound derived from NPEOs, surfactant was measured at concentrations up to 4.4 μ g L^{-1}. According to the water quality criteria in the EU, this reported concentration exceeds the maximum permissible concentration in ambient water of 1 μg L^{-1}

From an ecological point of view, the continuous use of APEOs will increase the level of pollution in the environment and pose a great risk to both aquatic life and human health. It is apparent that an alternative to APEOs must be found. The best substitute appears to be alcohol ethoxylates AEOs, which are less toxic than APEs in terms of their estrogenic effect. They are biodegradable and yet, in the environment, the intermediate product is less degradable than the parent compounds. Nevertheless, AEOs cannot replace APEOs in some industries; to achieve a similar efficacy, high levels of AEOs should be used (Campelle, 2002). Consequently, they will be more abundant in the WWTPs and could be released into the environment, depending on the performance of the treatment in WWTPs. The reported half-life for AEOs in soil was 30-40 days depending on the soil type and depth. Furthermore, for a given AE surfactant, the higher the number of ethylene oxides (EO) units results in less degradation of the surfactant (Krogh et al., 2003). In order to compensate for environmental concerns and to find efficient alternatives, (AE) are considered the best substitute for APEOs.

On the other hand, surfactant concentrations in grey water were higher than that in raw domestic wastewater because the former contains mainly wash water. Laundry effluent had the highest mean surfactant concentration, followed by kitchen and bath effluents. Although domestic detergents and cleaning materials contain biodegradable surfactants, strong binding of surfactants with soil may inhibit their breakdown (Kuhnt, 1993). Accumulation of surfactants from grey water may lead to water repellent soil with a significant effect on agricultural production and environmental sustainability. Similarly, Wallach et al. (2005) reported that soil water repellency developed under the continuous irrigation with treated sewage effluent in a semi-arid area. Therefore, increasing the use of insufficiently treated grey water may result in the expansion of water-repellent soil areas and negatively alter soil structure and texture, thus, increasing environmental pollution.

2.2.2. Effect of surfactants on soil properties

Due to their amphoteric nature, surfactants contain a large hydrophobic alkyl chain with a hydrophilic polar head (oxyethylen group). Depending on the molecule charge, surfactants are classified as anionic, cationic or non-ionic. Generally, the hydrophobic moiety reacts slightly with water molecules; however, the hydrophilic polar head strongly reacts with water molecules and may cause a reduction in surface tension and increase water infiltration into soil. For that reason, surfactants have been used as soil conditioners to artificially improve soil structure and infiltration ability (Mustafa and Letey, 1969). The purpose of these wetting agents is to decrease the solid-liquid contact angles and to increase water flow and soil hydro-physical properties (Pelishek et al., 1962; Miyamoto, 1985). Surfactants as detergents are similar in their chemical group to those detected in municipal wastewater; however, they differ in other aspects such as chemical structure and some physicochemical properties. Typically, detergent surfactants are evaluated in terms of their detergency in water and their effect on soils.

Studies show that grey water contains detergents such as boron at a concentration of 1.3 mg L^{-1}. Due to the toxicity of boron at fairly low concentrations, this exceeds the recommended concentration in irrigation water at 0.5 mg L^{-1} for citrus trees and 2 mg L^{-1} for bell peppers. Because of the extensive use of boron for industrial purposes such as a whiting agent in many laundry detergents, high concentrations of boron are found in the grey water. Therefore, long term irrigation with grey water is more likely to negatively affect plant growth (Wiel – shafran, 2006). An increase in hydraulic conductivity may cause an increased infiltration rate. The main factors affecting soil hydraulic properties in the presence of surfactants could be the solution surface tension and the solid-liquid contact angle (Pelishek et al., 1962).

Hydraulic conductivity is an essential soil property in evaluating the potential risks for widespread groundwater contamination by different types of contaminants. Due to the larger pore size in soils with high hydraulic conductivities, the leaching potential of contaminants is likely to increase. Consequently, irrigation with grey water leads to groundwater contamination as a result of increasing soil hydraulic conductivity. Reusing surfactant rich water in irrigation washes the fine particles causing a reduction in surface tension. This leads to an increase in the hydraulic conductivity and a change in soil structure; hence, the soil becomes water-repellent. Consequently, water retention decreases and the water transport increases.

The problem of water repellent soils is important; therefore, many studies investigated the causes of water repellence in soil. These studies show that in arid and semi-arid areas, where grey water is used as a substitute for fresh water, water repellence is more likely. They observed changes in the capillary rise in soil irrigated with grey water containing surfactants. Using anionic and non-ionic surfactants individually or as mixtures results in a reduction in the capillary rise and increases the hydrophobicity of soil. That was attributed to the adsorption of the tested surfactants in soil. In the case of anionic surfactants, negative charges interact with a positively charged soil surface leading the alkyl chain extending into the aqueous medium. However, in the case of non-ionic surfactants, the hydrophilic head, namely, ethylene oxide binds with the soil surface via hydrogen bonding causing the alkyl chain to project towards the porous medium (Yuan and Jafvert, 1997). Therefore, the prolonged use of insufficiently treated grey water results in an expansion of the water-repellent soil areas and adversely influences the soil structure and texture, which increases the leaching potential of contaminants in soil.

Similarly, Doerr et al. (2000) reported that surfactants have the ability to displace hydrophobic compounds in soil and render the particle surface wettable. After rainfall or an irrigation event, the hydrophobic compounds may leach deeper in soil; immediately after drying, surfactants remain on the soil surface causing it to become hydrophobic, which leads to water repellency (Lehrsch and Sojka, 2011).

2.2.3. Effect on soil pH

It is evident that grey water irrigated soil has a lower pH value (8.2) when compared to fresh water irrigated soil. Also, higher pH values have the ability to dissolve organic matter in soil. This leads to an increase in the dispersion of soil due to the ability of laundry detergents to remove dirt from clothes. As a result, there is a decrease in soil structure because of the separation in the soil particles (Wiel – shafran, 2006). Over time, the elevation in pH values could potentially alter the soil environment and make it alkaline. This, in turn, will make the soil environment unfavorable to microorganisms. Therefore, the leaching of dissolved organic matter is more likely to occur. DOM is considered a source of nutrients for plants and the loss of DOM could limit plant growth. This is important because after the application of manure, soil pH levels rise and the hydroxyl groups around the clay minerals become ionized, hence, increasing the extent of cation exchange capacity resulting in alkaline soils. Thus, diluting grey water is highly recommended to avoid an increase in pH of the soil. There are several kinds of surfactants used in personal cleansing and in household and industrial cleaning products, such as anionic, non-ionic, cationic and amphoteric (SDA, 2004). Among these, non-ionic surfactants are the most common in the environment. They are described briefly below.

2.2.4. Effect of surfactants on herbicide mobility

Herbicides are compounds, which are applied to control weeds in croplands and in residential areas. Pesticides degrade in soil-water systems due to microbial activities; however, they are persistent and can transport to water bodies in surface runoff and subsurface flow. Several pesticides are frequently used and many have been detected in soil/water. Atrazine, metolachlor and metribuzin are commonly used pesticides in North America and around the world.

Surfactants are widely used in the field of bioremediation due to their ability to increase recovery of organic chemicals during the process of soil washing through two mechanisms. Firstly, surfactants decrease the surface tension and the capillary forces that capture the residual chemicals. As a result, the residual chemicals in the presence of surfactant are reduced and move down in the soil profile. Secondly, surfactants are capable of forming dynamic aggregates known as micelles. Above a critical surfactant concentration known as the critical micelle concentration (CMC), the hydrophobic part of the surfactant molecule will aggregate together forming the micelle core and the hydrophilic part will protrude to the aqueous phase on the exterior. Subsequently, the hydrophobic chemicals are solubilized due to their presence in the core of the micelles, which serves as a compatible environment for these chemicals; the process of incorporation of these molecules into a micelle is known as solubilization. However, below CMC, surfactants exist in the monomeric form and enhancement of organic solubility is unlikely to occur (Cheah et al., 1998). However, the apparent solubility of several hydrophobic organic compounds can be increased in the presence of certain surfactants even below CMC; instead of solubilization, the insoluble organic compounds are partitioned into the organic carbon fraction of the dissolved organic matter. Above CMC, the apparent solubility of hydrophobic organic compounds increases significantly due to the process of solubilization. For example, Pennell et al. (1993) indicated that the aqueous solubility of dodecane increased by six orders of magnitude in the presence of the surfactant polyoxyethylene 20 sorbitan monooleate.

The release of pesticides from soils is a surfactant dependent process. Both non-ionic surfactants Triton X-100 and Tween 80 at higher concentrations than CMC, increased desorption of the hydrophobic pesticide lindane from soil. However, the anionic surfactant Sodium Dodecyl (SDS) exhibits an insignificant effect. This difference in behavior reflects the role of the surfactant hydrophobicity on desorption (Quintero et al., 2005). Further, non-ionic surfactants at a concentration of 0.2% could increase the adsorption of liadane and diuron. At higher concentrations of 0.5% to 1.0%, the surfactants led to a decrease in adsorption of those two pesticides (Huggenberger et al., 1973; Foy, 1992).

Steurbaut (1994) reported that the solubilisation of a given pesticide in the micelle system results in a restriction in the interactions between the soil and the pesticide. Therefore, this could contribute to higher mobility by using non-ionic surfactants possessing longer ethoxylate units. Bayer (1967) studied the effect of 23 surfactants (4 anionic, 6 cationic and 13 non-ionic) on the depth of leaching of urea herbicides in a sandy clay loam soil. According to his results a 1% concentration of each surfactant (1 anionic, 11 non-ionic, and 2 cationic) increased the depth of leaching of diuron. Increasing the amount of anionic surfactants up to 10% resulted in further increases in the depth of leaching. In the case of cationic and non-ionic surfactants, the movement of pesticides decreased. A study with 3 non-ionic surfactants at a concentration of 2% resulted in increased movement of trifluralin and oryzalin in sandy soil. The addition of surfactants to dry soil had more effect on herbicide movement than in wet soil (Koren, 1972). Further, Huggenberger et al. (1973) stated that the distribution of lindane and diuron in the soil column was at its maximum at shallower depths, when non-ionic alcohol ethoxylates were used at lower concentrations.

Kan and Tomson (1990) observed that DDT moved 1000 times faster in the presence of non-ionic surfactant X-100 at a concentration of 2000 mg L^{-1}. Foy (1992) found that atrazine movement went deeper when the soil was pre-leached with water. Sanchez-Camazano et al. (1995) investigated the effect of three different concentrations (0.04, 5 and 50 g kg^{-1}) of the non-ionic surfactant Tween 80 on the mobility of diazinon, atrazine and metolachlor in soil and indicated that the downward movement of atrazine and diazinon was reduced in soil; this effect increased with increasing surfactant concentrations. However, the mobility of metolachlor decreased at concentrations of 0.04 g kg^{-1} and increased slightly at concentrations 5 and 50 g kg^{-1}. Moreover, adding Tween 80 at 50 g kg^{-1} to the leaching water increased the mobility of the three hydrophobic pesticides.

Abu Zreig (1999) studied the influence of surfactants on the sorption of atrazine in soil and found that in the presence of sulphonic surfactants, the adsorption of atrazine increased considerably in soils. This increase is directly proportional to the concentration of the surfactant. In fact, the application of the sulphonic surfactants at concentrations of 3000 mg L^{-1} resulted in a significant increase in K_d values of atrazine in loam and sandy loam soils. Inversely, the effect of non-ionic surfactants is concentration dependent. Basically, in the presence of non-ionic surfactants at high concentrations, atrazine sorption was slightly increased. However, at low concentrations, non-ionic surfactants have shown a tendency to reduce the affinity of atrazine to soil. A lysimeter study was performed by Nilufar (2005) to examine the influence of low surfactant levels, commonly present in semi-treated and untreated municipal wastewater (LAS anionic and NP degradable compound of non-ionic), on the movement of three agricultural herbicides, atrazine, metolachlor, and metribuzin. The results show that irrigation water with a concentration of 12 mg L^{-1} of LAS and NP had almost no effect on the leaching of atrazine, metolachlor, and metribuzin. On the other hand, laboratory experiments revealed that in the presence of LAS, the partition coefficients (k_d) values increased for atrazine and metribuzin; however, the sorption was not significantly changed for the three herbicides in the presence of NP. Tao et al. (2006) carried out experiments to determine the effect of surfactants at low concentrations on the sorption of atrazine by natural sediments, and found that at surfactant concentrations ranging from 0 to 20 mg L^{-1}, anionic and cationic surfactants substantially decreased the sorption of atrazine. Whereas, it was found that non-ionic surfactants have reduced the adsorption of atrazine at concentrations equal to or less than 1 mg L^{-1}, and increased adsorption at higher concentrations. Interestingly, low concentrations of surfactants were confirmed to mobilize atrazine in sediments, which indicates that even at low concentrations, surfactants are potentially capable of mobilizing toxic substances that have been adsorbed by sediments.

Since non-ionic surfactants are known for their ability to release pesticides from aged soils, Mata Sandoval et al. (2000) reported that Triton X-100 showed good desorption efficiency of pesticides from soil by replacing the pesticide on the sorption sites on soil particles and releasing it from the soil. Xiarchos and Doulia (2006) stated that the ability of solubilizing polar compounds is positively linked to hydrophilicity, and this hydrophilicity is known to be governed by the number of oxyethylene groups (EO) in the molecule, i.e., the greater the number of EO groups, the more hydrophilic the surfactant (Jafvert et al., 1994). Further, Sun et al., 1995 reported that micelles in the aqueous phase act as an effective partitioning medium for hydrophobic organic compounds (HOCs); therefore, they reduce their affinity to sorb to soil. This was confirmed by the lower K_d values obtained in their study. Similarly, Chappell et al. (2005) investigated the effect of Brij 35 on the adsorption of atrazin and found that Brij 35 competes with atrazin for sorption sites in the soil and the presence of micelles has the potential to dissolve atrazin. The release of the pesticide, phenanthrene, from contaminated soils was increased primarily in the presence of alcohol ethoxylates surfactants such as Alfonic 810-60 and Novel II at concentrations below CMC (Aronstein et al., 1991).

As a result of the amphiphilic nature of surfactants, they can solubilize hydrophobic compounds in the environment (Huggenberger et al., 1973; Kan and Tomson, 1990; Aronstein et al., 1991; Rodriguez-Cruz et al., 2004). Generally, unlike cationic and anionic surfactants, non-ionic surfactants increase the downward movement of pesticides in soil. This is due to lower CMC values, a higher level of surface-tension reduction and their significant solubilization capacity in dilute solutions (Paria, 2008). More specifically, Sanchez-Camazano et al. (1995) reported that non- ionic surfactants at high concentrations effectively increased the mobility of the herbicide, metolachlor, in soil; however, at low concentrations of surfactants, metolachlor mobility was reduced. Similarly, Katagi (2008) indicated a greater mobility of pesticides in leached water at high concentrations of non-ionic surfactants. Further, Katagi (2008) confirmed that both non-ionic and anionic surfactants mostly increased the downward mobility of pesticides and some cationic surfactants markedly reduced the mobility of antibiotics.

To date, very few studies have investigated the sorption of antibiotics in a soil-water surfactant system. Hari et al. (2005) indicated that, unlike acetaminophen and carbamazepine, nalidixic acid and norfloxacin exhibit low affinity to soil in the presence of the non-ionic surfactant NP9, indicating that the sorption behavior of the two groups of antibiotics is not ruled by their solubility or log K_{ow}. Therefore, Muller et al. (2007) reported that wastewater irrigation was found to enhance the mobility of contaminants such as pesticides. They also stated that the presence of surfactants in irrigation water is considered a key factor in promoting the leaching potential of pesticides. Additionally, non-ionic alcohol ethoxylates (AE) are found to enhance the mobility of pesticides when applied at high (*vs.* low) concentrations to soil columns (Huggenberger et al., 1973). Chefetz et al. (2008) studied the effect of irrigation with secondary treated wastewater (STWW) on the environmental behavior of pharmaceutical compounds in soil columns and reported that naproxen was mobile in soil irrigated with STWW. This behavior was the result of competition between DOM, which is present in wastewater, and naproxen for binding sites. Kulshrestha et al. (2004) arrived at a similar conclusion when they stated that dissolved natural organic acids, such as humic acids, may compete with clay for oxytetracycline and thus, enhance its mobility in the soil profile.

2.2.5. Nonionic surfactants

Nonionic surfactants do not ionize in aqueous solution, because their hydrophilic group is of a non-dissociable type, such as alcohol, phenol, ether, ester, or amide. A large proportion of these non-ionic surfactants are made hydrophilic by the presence of a polyethylene glycol chain, obtained by the polycondensation of ethylene oxide. Non-ionic surfactants have the advantage over ionic surfactants since they are compatible with all other types of surfactants and their properties are slightly affected by pH (Effendy and Maibach, 2006). Nonionic surfactants are used as emulsifiers, solubilizing and wetting agents. They have various applications in the food, cosmetic, paint, pesticides, and textile industries. Among surfactants, non-ionic surfactants such as alcohol ethoxylates (AEOs) and alkylphenol ethoxylate (APEO) are widely used in cleaning products, detergents and the textile industry; they are likely to be detected in urban sewers (Conn et al., 2006; Loyo-Rosales et al., 2007; Stuart et al., 2012).

It is evident that nonionic surfactants are widely used in large quantities in the textile industry due to their ability to lower the interfacial tension of water and other materials to increase the penetration of processing solutions in textiles. Surfactant concentrations in wastewater can vary significantly, depending on the procedure. The reported concentrations are about 15 mg L^{-1} in a silk and lycra printing plant and up to 800 mg L^{-1} for wool scouring and up to 2000 mg L^{-1} for desizing wastewaters (Bisschops and Spanjers, 2003). Therefore, Campbell (2002) reported that there are two challenges facing the textile industry. First, the cost issues associated with certain alternatives to anionic surfactants. Secondly, poorly treated textile effluents containing high amounts of non-ionic surfactants has the tendency to increase the level of BOD loadings following their discharge into the effluents in the WWTP. Moreover, the facilities which used biodegradable surfactants as alternatives of APEOs are found to be the main cause of this problem. Apparently, in textile wet processing operations, the normal level of BOD started from 300 ppm upwards; however, the pretreatment BOD in WWTPs requires a level of BOD of 250-300 ppm. In order to meet the requirements for the pretreatment BOD, some facilities decided to limit the use of safer alternatives and use APEOs. Therefore, it is anticipated that there will be higher amounts of the less biodegradable surfactants discharged in the final effluents.

Belonging to nonionic surfactants, Alcohol ethoxylates (AEs) account for the largest group, by volume, of nonionic surfactants produced worldwide (Talmage, 1994). The demand for detergent grade alcohols in 2010 grew about 3.1%, from 1500 kilotonnes in 1998 to 2100 kilotons in 2010 (Colin Houston & Assoc., 2000). Alcohol ethoxylates are structurally based on high linearity alcohols as the predominant type. It was estimated that 90% of AE used in North America are based on primary linear alcohols. AE are less sensitive to water hardness than other non-ionics; they are particularly effective at removing oily soils, and produce relatively low levels of foam. The structure of the hydrophobic part of the AE molecule is formed from fatty alcohols with chain lengths between C_9 -C_{18}. However, the hydrophilic part of the molecule contains an ethylene oxide ranging from 2 - 100 units. Many alcohol ethoxylates are available on the market. Alcohol ethoxylates have the following standard structure (Eq. 2.3):

$$CH_3\text{-}(CH_2)_n\text{-}CHR\text{-}CH_2\text{-}(O\text{-}CH_2\text{-}CH_2)_m\text{-}OH \qquad \text{Eq. 2.3}$$

Where n = 5-15, m = 2-100, R = H or n-alkyl

Alcohol ethoxylates undergo biodegradation. Basically, the factors influencing the rate and extent of biodegradation are the type and extent of branching in the alkyl chain, the extent of incorporation of propylene oxide in the ethoxylate chain, and the length of the ethoxylate chain. Biodegradation is delayed by the presence of a high degree of branched alkyl chains, a secondary alkyl chain structure, the addition of more than three equivalents of propylene oxide units into the ethoxylate chain, and by the length of the ethoxylate chain by more than 20 units. The primary biodegradation intermediates of AE are polyethylene glycols (PEG) that have been found to be less toxic than the intact parent surfactants to aquatic organisms. Generally, toxicity increases when alkyl chain length increases. Further, branched alkyl chains are less toxic than linear alkyl chains.

In sewage effluents, AEs are subject to biodegradation and then produce intermediates which are generally polyethylene glycols (PEG) and carboxylic aerobic metabolites i.e. carboxylated PEGs. Furthermore, in the US, the final effluents concentrations of AEs ranged from 8-509 µg L^{-1} in Ohio and 441 µg L^{-1} in Sadalia. The reported concentrations exceeded the predictable environmental concentration (PEC). Based on the chronic effect value for AE which is known as predicted no effect concentration (PNEC), the corresponding value for AEOs is equal to 110 µg L^{-1} compared to 1 µg L^{-1} for APE. The primary process for commercial AE blends is biodegradation. The degradation rate of the metabolites depends on the length of the molecule. In addition, slow biodegradation of PEGs was observed compared to the parent AE. Likewise, Soares et al. (2008) indicated that the metabolites of AEs are less soluble in water and they have an affinity to adsorb to sludge solids. On the other hand, nonionic surfactants are known to readily bind to several proteins and membranes, which modify the protein structure and the degree of permeability of the cell membrane. In this regard, Cserhati (1995) observed various effects of nonionic surfactants on several biological activities. He indicated that surfactants are capable of interacting with bioactive macromolecules, such as proteins, peptides, amino acids, and membrane phospholipids.

In terms of the bioaccumulation, AEs are rapidly absorbed and distributed throughout the body by fish within two hours, then the parent compounds are metabolized into the body in 24 hours. Depending on the degree of ethoxylation, bio concentration factors are found to be higher for the AE with shorter EO chains. Similarly, the toxicity of nonionic surfactants to both aquatic and terrestrial organisms has been documented (Krogh et al., 2003).

Compound of interest

Brij 35

Polyoxyethylene-lauryl ether (Fig 2.2) is one of the Alcohol Ethoxylates and it is used in the production of cleaning agents as well as in pharmaceutical formulations and for other industrial purposes.

$$H_3C-(CH_2)_{11}-O-(CH_2-CH_2-O)_n-H$$

Figure 2.2 Chemical structure of Brij 35 (Gao et al., 2002)

From the literature, the effects of detergent surfactants present in wastewater are of great importance since they affect the physical properties of soils. Few studies have investigated the impact of the presence of surfactants in wastewater on soil properties and on the transport of organic compounds in soils (Abu-Zreig, 2003; Foy, 1992). Therefore, more investigations are required to evaluate the risk of the presence of surfactants on the soil and water contamination when it is necessary to reuse waste water for irrigation.

2.3. Pharmaceutical antibiotics

During the last decade, antibiotics have been classified as a new class of emerging contaminants. Due to the widespread use of antibiotics for human and veterinary purposes, they are continuously released into environmental compartments such as streams, rivers, medical waste, discharge from wastewater treatment facilities, leakage from septic systems and agricultural waste storage structures, overland flow runoff, landfill with human and agricultural wastes and transport from agricultural lands previously applied with manure and slurry (Halling-sorenson et al., 1998; Kay et al., 2005; Michael et al., 2013).

Generally, antibiotics are large molecules, which vary widely in their physicochemical and biological properties. As a result of their high solubility and low biodegradability, they exhibit a low affinity for sorption, thus, enhancing their bioavailability. In addition, antibiotics are designed to be polar and hydrophilic, which can increase their occurrence in surface water bodies. Antibiotics exhibit a pseudo persistence (i.e. their high removal rates compensated with their continuous introduction in the environment) (Diaz-Cruz et al., 2003). Therefore, their prolonged impact is expected to negatively affect the receiving environments.

Antibiotics administered to humans and livestock are partially metabolised inside the animal. Therefore, they are more likely to be released in the form of the parent compounds and their metabolites (Boxal et al., 2001). It is estimated that up to 90 % of antibiotics are excreted without having been metabolized (Halling-Sørensen et al., 1998). Typically, animal wastes are applied to agricultural soils as a source of nutrients. In this way, they provide an input pathway of veterinary antibiotics into the environment. Since antibiotics differ in their structure and properties, more investigations are required to understand the extent of transport of these compounds in ground water.

2.3.1. Occurrence of Pharmaceutical antibiotics

The presence of pharmaceutical antibiotics in the environment is of great concern. Since the late 30s, antibiotics have been used in both humans and animals (Cromwell, 2000). Ultimately, their presence in the environment is positively correlated with their increasing production for human and animal consumption (Lindberg et al., 2005).

Overall, conventional wastewater treatment generally employs a primary, secondary and in some modern facilities, a tertiary step. Different biological and physicochemical processes are involved for each stage of the treatment. The importance of the primary treatment comes from the employment of the mechanical reduction of the solid content of the wastewater by filtration and sedimentation. The secondary treatment depends mainly on the biological process to remove organic matter and/or nutrients with aerobic or anaerobic systems. The best known method involves the conventional use of activated sludge (CAS). In this stage, the treatment plants with activated sludge utilize dissolved oxygen to enhance the growth of a biological floc that considerably eliminates the organic material and nitrogen at certain conditions (Batt et al., 2007).

Unlike hydrophilic antibiotics, the residues of the hydrophobic antibiotics are assumed to occur at higher concentrations in primary and secondary sludge treatment. This is probably due to their high degree of binding to solids. Therefore, they accumulate in the organic-rich sewage sludge (Le-Minh et al., 2010). Furthermore, Diaz-Cruz et al. (2003) reported that the removal of antibiotics from aqueous solutions onto solids can be achieved by ion exchange, complexation with inorganic metal ions and polar hydrophilic interactions. After sorption to suspended solids and activated sludge, antibiotics are removed by sedimentation and the successive discharge of the extra sludge. It is worthwhile noting that the more sorption to sludge, the higher the values of the sorption coefficient (K_d) of antibiotics employed in the removal process. Therefore, one must caution the use of sludge as fertilizer on agricultural soils in order to avoid increasing the input of antibiotics to the environment. For that reason, European countries have banned the spread of sludge in soil (Micheal et al., 2013).

The removal efficiency of antibiotics is highly dependent on the properties of each class of these compounds and ranges from nearly complete to very little. However, there is a lack of information in the literature about the fate and transport of antibiotic residues during wastewater treatment. A study by Le-Minhet et al. (2010) revealed that the differences in the reported removal efficiencies of antibiotics could be due to the limitations in the techniques used to calculate the mass balance. In this regard, studies have indicated the presence of significant variations of antibiotics loads in the influent on the short term (Gobel et al., 2005; Khan and Ongerth, 2005). Attention to efficiency is required to compare the final concentrations in the effluents based on the data previously taken from the influent.

Several studies have been conducted to investigate the occurrence of these antibiotics in the US, Canada and Europe. For example, in Wisconsin, they collected many samples from different sources such as activated sludge plants, oxidation ditches and lagoons; they found that the most abundant antibiotics in 80 % of the samples were tetracycline and trimethoprim with concentrations of (0.52 and 0.17 µg L^{-1}) and (0.33 and 0.17 µg L^{-1}) in the influent and the effluents, respectively (Karthikeyan and Meyer, 2006). Similarly, in New York, Batt et al. (2007) reported that sulfamethoxazole concentrations were (0.72 -2.8 and 0.22-0.68 µg L^{-1}) and tetracycline levels were (0.32 and 0.29 µg L^{-1}) in the influent and the effluents, respectively. In Canada, samples of treated effluents from eight WWTPs in five Canadian cities were analyzed and it was reported that 31 antibiotics were detected (Miao et al., 2004). Ciprofloxacin, ofloxacin, sulfamethoxazole, sulfapyridine and tetracycline were the most frequently detected with concentrations of 0.4, 0.506, 0.871, 0.228 and 0.977 µg L^{-1}. Furthermore, the highest concentration levels of ciprofloxacin, ofloxacin and sulfamethoxazole were detected in both influent (85-100%) and effluent samples (79-100%) in Spain with maximum concentrations of 5.3, 2.2 and 1.3 mg L^{-1} for raw sewage, and 1.9, 2.8 and 0.5 mg L^{-1} in output wastewater, respectively (Bueno et al., 2012). Similar values have been reported for ofloxacin and sulfamethoxazole in Taiwan (Yu et al., 2009) and for ciprofloxacin in the UK (Kaspryk-Hordern et al., 2009).

Antibiotics originating in the livestock industry have been detected in surface waters in Canada (Lissemore et al., 2006), the USA (Kolpin et al., 2002; Watkinson et al., 2009), Europe (Feitosa-Felizzola and Chiron, 2009; Hirsch et al., 1999) and Asia (Managaki et al., 2007; Minh et al., 2009). A recent survey of treated drinking water across the United States indicated that antibiotics were present in over half of the water supply. There is increasing evidence of antibiotics reaching surface and ground water from CAFOs and from manure applied on agricultural soils (Davis et al., 2006; Kemper, 2008; Thiele Bruhn, 2003; Watanabe et al., 2010; Watanabe et al., 2008).

It is estimated that the total manure produced from Canadian livestock is 177.5 million tons annually (Hofmann and Beaulieu, 2006). The corresponding amount of manure produced in USA is estimated to be more than 130 million tons annually (Dolliver and Gupta, 2008). In the United States, land application is the most common method for manure disposal following its storage in lagoons or pits (Chee-Sanford et al., 2009). As a result of this disposal method, soil and water contamination may occur (Kuchta et al., 2009).

The results samples analyzed from liquid waste at hog and poultry AFOs in six states in the US indicated that chlortetracycline, sulfamethazine, and lincomycin were the most frequently detected antibiotics. In addition, the estimated concentrations of individual antibiotic compounds from the hog-lagoon waste ranged from <1 to more than 1000 µg L^{-1} (Meyer et al., 2003). Likewise, in the hog CAFOs in Iowa, one or more of the following antibiotic compounds were detected in four groundwater samples (chlortetracycline, oxytetracycline, lincomycin, sulfamethazine, trimethoprim, sulfadimethoxine, and the dehydrated metabolite of erythromycin). In Swiss surface waters, sulfamethazine and other classes of antibiotics used in livestock facilities were detected due to runoff from land-applied manure (Alder et al., 2001). However, residues of sulfonamide antibiotics were detected in four samples collected from an agricultural area, with two samples showing sulfamethazine at concentrations of 0.08 and 0.16 µg kg^{-1}.

Wanatabe et al. (2010) indicated that samples of sediments from a lagoon in a dairy farm in the US were found to contain several antibiotics such as sulfamethazine (36 µg kg^{-1}), total chlortetracycline (176 µg kg^{-1}), oxytetracycline, and tetracycline (42 µg kg^{-1}) at concentrations of 36, 176, 109 and 42 μg kg $^{-1}$, respectively. However, in surface water samples, they detected sulfamethoxazole (6.2 μg kg $^{-1}$), oxytetracycline (25 μg kg $^{-1}$), tetracycline (8.8-105 μg kg $^{-1}$), and epitetracycline (163 μg kg $^{-1}$). Furthermore, analysis of many samples from groundwater under manure-treated fields revealed the existence of sulfadimethoxine and sulfamethazine in monitoring wells close to a field receiving lagoon water at concentrations ranging from 0.029 to 0.11 μg L $^{-1}$. They attributed that to the high infiltration rate in soil due to the closeness of the outlet valves of the lagoon-water flood irrigation system.

Generally, feces and urine excrements are the main sources of antibiotics in the animal production areas. They spatially accumulate in a heterogeneous pattern resulting in an observed variability of the reported concentrations of several antibiotics in soils. In sediment samples from dairy farms, sulfonamides (mainly sulfadimethoxine) and tetracyclines were frequently detected in soil surface samples. Similarly, oxytetracycline and erythromycin were measured at high concentrations from 188 to >1000 μg kg^{-1}. Furthermore, concentrations of sulfadimethoxine (5.8 -457 μg kg $^{-1}$) and tetracycline (6.2-73 μg kg $^{-1}$) were among the most frequently detected antibiotics in surface samples of hospital pens at dairy farms. The presence of other antibiotics such as oxytetracycline (11 and 18 μg kg $^{-1}$), and epitetracycline (11 μg kg $^{-1}$) at hospital pens has been reported (Wannataba et al., 2008). Collectively, some classes of antibiotics such as tetracyclines (TCs), sulfonamides, macrolides and ionophores have been detected at concentrations up to 0.7 mg L^{-1} in hog waste lagoons (Tolls, 2001; Campagnolo et al., 2002, Key et al., 2004; Himmelsbach and Buchberger, 2005).

2.3.2 Sources and Pathways

Municipal wastewater is one of the primary sources of antibiotics in the environment. Therefore, it is not surprising that different classes of antibiotics have been detected in the effluent of wastewater treatment plants (WWTP) indicating that primary and secondary treatments employed by conventional treatment systems are not efficient in eliminating these compounds (Carballa et al., 2004).

Overall, the common groups of antibiotics, which are frequently detected in wastewater, are macrolides (erythromycin), tetracyclines (oxytetracycline and tetracycline) and sulfonamides (sulfamethoxazole). Therefore, it is worth understanding the fate of these compounds in wastewater treatment plants to evaluate the risk of surface water pollution. Basically, there are several factors influencing the abundance of antibiotics in WWTP influents and effluents, including the amount consumed of a particular compound, the type of removal treatment employed and the overall efficiency of the WWTP. For example, in China, Peng et al. (2006) reported that the concentration of sulfamethoxazole in sewage influent was 5450-7910 ng L^{-1} with 100 % removal efficiency; however, in Taiwan, the detected concentration in the influent ranged from 500 to 10,000 ng L^{-1} with the removal efficiency ranging from 65- 96% after the biological treatment (Yu et al., 2009). Different removal efficiencies of sulfamethoxazole have been reported; for example, 81% (initial concentration 1090 ng L^{-1}) (Yang et al., 2005), 69-75% (initial concentration in the range 13-155 ng L^{-1}) (Pailler et al., 2009), 68.2- 95.7% (initial concentration in the range 146-355 ng L^{-1}) (Li et al., 2009) and 93% (initial concentration in the range 3000 ng L^{-1}) (Watkinson et al., 2009). Nevertheless, lower removal rates of 20-24% have been also reported (Brown et al., 2006; Ternes et al., 2007).

On the other hand, Watkinson et al. (2007) reported that tetracycline is one of the most frequently detected antibiotics in wastewater. Due to the high sorption affinity of TCs, it is important to investigate their fate in WWTPs. It is evident that the removal efficiency reported in the literature varies significantly. In Colorado, Yang et al. (2005) indicated that tetracycline was removed by 85% in a WWTP. Whereas, Li and Zhang (2011) reported removal rates of 24- 36% at two plants while Karthikeyan and Meyer (2006) reported higher removals (67.9-100%). The removal rates for chlortetracycline as reported by Li and Zhang

(2011) were in the range of 82% and 85%. More specifically, tetracyclines favors forming complexes by chelating with calcium and similar ions; thus, these stable complexes can easily bind to suspended matter or sewage sludge (Drewes, 2008). Furthermore, Kim et al. (2005) concluded that sorption is considered the major removal mechanism in activated sludge. Additionally, lack of biodegradation of TCs was confirmed in their study. These properties might explain why tetracyclines are detected in many cases at low concentration levels (ng L^{-1}) in treated secondary effluents.

The concentrations of antibiotics, sulfamethazine, oxytetracycline, tetracycline, chlortetracycline, and erythromycin were below the detection limit at (0-30 cm depth) in soil samples collected from lactating cow freestall soils and from lactating cow exercise yard soils; and yet they were intermittently found in surface samples. However, in the case of sulfamethoxazole, measurable concentrations were detected in both surface and soil samples. The surface and soil samples from the hospital pen were analysed and concentrations of sulfadimethoxine and tetracycline were detected at concentrations ranging from 11 to 30 µg kg $^{-1}$. The sporadic administration and spatial variability of antibiotics lead to different patterns of excretion, which affect their occurrence accordingly. Generally, the occurrence of various antibiotics in soil samples indicates the difference in the mobility of antibiotics in the subsurface environment. The presence of antibiotics in wells near the feed and manure solids storage areas, and near possibly leaking, buried flush water pipelines was reported; sulfamethazine was detected at concentrations ranging from 0.088 to 0.14 µg kg $^{-1}$. Similarly, limited amounts of tetracyclines (0.08-0.4 µg L^{-1}) were detected in a few wells. However, tylosin and sulfadimethoxine were detected sporadically in groundwater below animal production areas. The occurrence of sulfonamides in drinking water wells nearby CAFO has been reported in Idaho where concentrations from 0.076 to 0.22 µg L^{-1} of sulfonamides were detected (Batt et al., 2006). This indicates the low affinity of these antibiotics to soil which results in their considerable mobility.

The occurrence of tetracyclines and sulfamethazine (sulfonamide group) in sandy soils ammended with liquid manure was investigated and the results showed that the highest detected concentrations were 27 µg kg $^{-1}$ (OTC), 443 µg kg $^{-1}$ (TC), 93 µg kg^{-1} (CTC), and 4.5 µg kg $^{-1}$ (sulfamethazine) in the top 0–30-cm soil. TCs concentrations exceeded EMEA (European Agency for the Evaluation of Medicinal products) permissible concentrations of 100 µg kg $^{-1}$ at more than three tested agricultural fields (Sarmah et al., 2006). The analysis of samples from agricultural soils showed that TCs detected at concentrations of 450– 900 µg kg $^{-1}$. Conversely, Runsey et al. (1977) stated that no antibiotic residues were detected in manure applied to pasture and soil. This conclusion may be attributed to the lack of up to date analytical methods and instrumentation at that time. Lissemore et al. (2006) indicated that run-off from agricultural soil in Southern Ontario caused the contamination in the river surface water by various antibiotics such as monensin at concentrations from 6.2-1172 ng L^{-1} and several sulfonamides at concentrations from (0.2 to 408 ng L^{-1}). They add that monensin concentrations were affected by the presence of dissolved organic carbon; however, the presence of nitrate and phosphate ion concentrations had no effect.

Antibiotics belonging to different groups such as macrolides, sulfonamides, and tetracyclines were detected in river water in England at concentrations of 1 µg L^{-1} (Watts et al., 1982). Following this, a variety of other antibiotics were also detected in surface water in concentrations up to 1 µg L^{-1} (Richardson and Bowron, 1985; Pearson and Inglis, 1993; Ternes, 1998; Hirsch et al., 1999). The sporadic use of some antibiotics for nontherapeutic purposes resulted in their occurrence in WWTP effluents. This has been observed for the antibiotic chloramphenicol, which is used to cure severe meningitis in humans. Although its use for veterinary purposes has been banned in Europe since 1995, chloramphenicol is still detected in sewage treatment plant effluent and small rivers in Southern Germany at concentrations of 0.56 and 0.06 µg L^{-1} respectively (Hirsch et al., 1999) as a result of its use in fattening farms.

Veterinary antibiotics have also been detected in groundwater (Holm et al., 1995; Hirsch et al., 1999; Hamscher et al., 2000). As a matter of fact, most of the detected antibiotics in ground water were obtained primarily from the extensive use of antibiotics in agricultural areas with a large number of fat stock farms or sewage irrigation fields. However, Hirsch et al. (1999) indicated that none exceeded the limit of 0.02–0.05 µg L^{-1}. Basically, sulfonamide antibiotics are not administered to humans and the only reason for their occurrence is their extensive use in veterinary applications. For example, sulfamethazine was detected at concentrations of 0.08 and 0.16 µg L^{-1} in groundwater samples collected from an agricultural area. Additionally, Hamscher et al. (2000) reported the presence of chlortetracycline, oxytetracycline, tetracycline and tylosin at the limit of detection of 0.1–0.3 µg L^{-1} in leachate samples collected from agricultural land. Collectively, the analysis of groundwater samples near swine farms in the US showed measurable concentrations of several classes of antibiotics such as tetracycline, macrolide, b-lactam, sulfonamide (Campagnolo et al., 2002). In groundwater influenced by agricultural activities, sulfamethoxazole (up to 0.47 µg L^{-1}), and lincomycin (1.4 µg L^{-1}) have been detected in beef feedlots and swine lagoons. However, Watanabe et al. (2010) reported higher concentrations of sulfamethazine in their study compared to the literature, whereas, sulfamethoxazole was barely detected. Thus, it appears that sulfonamides, in lagoon waters, are readily transported into shallow groundwater, but do not persist in soil or at the land surface. On the other hand, tetracyclines have a strong affinity for sorption; consequently, they are more likely to persist at the soil surface where they dissipate overtime. Therefore, the continuous application of lagoon water and manure as fertilizers increase the possibility of antibiotics transportation into groundwater triggered by recharge from irrigation or rainfall

Typically, the use of pharmaceuticals in aquaculture is a major input pathway to environmental waters. It is estimated that about 70% to 80% of the administered drugs in fish farms may be released into the aquatic environment (Walsh, 2008). As the favorite antibiotic in aquaculture, oxytetracycline, was detected at a very high concentrations of 285 mg kg $^{-1}$ in sediments indicating that large amounts of the drug was discharged regularly as parent compounds into the environment (Samuelsen et al., 1992). Furthermore, concentrations of oxytetracycline residues ranging from 500 to 4000 µg kg^{-1} were measured in marine sediment following chemotherapy treatment in fish farms in the US (Capone et al., 1996).This is not to mention the use of antibiotics for production purposes in horticulture and apiculture (Kummerer, 2004).

The overall degree of antibiotic movement in soil results from three important processes: sorption, degradation and leaching. Basically, these processes are controlled by the physical and chemical properties of the antibiotics, such as molecular structure, hydrophobicity, water solubility, dissociation constants, and sorption–desorption processes, as well as the stability and the degree of affinity to the soils and the partitioning coefficients at different pH conditions. Rabolle and Spliid (2000) observed that most of antibiotics which are widely used in swine farms as growth promoters such as oxytetracycline, tylosin, metronidazole and olaquindox remained in the surface of the soil column. The calculated sorption coefficients for oxytetracycline and tylosin were a few orders of magnitude greater than metronidazole and olaquindox, suggesting that a higher binding ability of these compounds could potentially affect their mobility in the following order metronidazole > olaquindox > tylosin > oxytetracycline. Likewise, Engels and Winckler (2004) reported that after the application of liquid manure containing tetracycline hydrochloride to humous sandy soil, no mobility of this antibiotic was observed. This immobility could be attributed to the reported higher sorption coefficient values for this compound (Tolls, 2001; Allaire et al., 2006; Carlson and Mabury, 2006). Generally, antibiotics adsorption to soil is the primary mechanism limiting antibiotic losses from manure-amended agricultural land. Furthermore, Wszolek and Alexander (1979) stated that the sorbed portions of a given chemical are more resistant to degradation than the non-sorbed fractions. Consequently, sorption by soil organic matter is found to reduce the biodegradation of polycyclic aromatic hydrocarbons that would otherwise readily break down. Therefore, strong adsorption inhibits the microorganisms from degrading oxytetracycline in soil; this suggests that oxytetracycline is persistent in soil compared to other antibiotics, such as sulfonamides. This is attributed to its high affinity to bind to soil particles (Manilal and Alexander, 1991).

However, in some cases, leaching has been observed. For instance, dissolved organic carbon (DOC) has potentially increased the movement of organic pollutants by increasing the apparent solubility of hydrophobic contaminants such as monensin due to adsorption competition (Chiou et al., 1986; Flores-Cespedes et al., 2002). In addition, the presence of monensin in surface water has been correlated to the dissolved organic carbon. However, the occasional loss of dissolved chlortetracycline indicates its high affinity to soil (Lissemore et al., 2006). In order to explain the high affinity of tetracyclines to soil, it is important to consider the fact that these compounds are pH dependant. Stephens et al. (1956) reported that tetracycline, oxytetracycline and chlorotetracycline have similar pKa values, which is consistent with their chemical structure. Basically, there are three functional groups for tetracycline: tricarbonyl methane (pKa 3.3); dimethyl ammonium cation (pKa 9.6) and the phenolic diketone (pKa 7.7). At environmentally relevant pH values, the presence of multiple ionizable functional groups in TCs molecules indicates that they may exist as a cation $^{+\,0\,0}$, zwitterion $^{+\,0}$, or as a net negatively charged ion $^{-00}$ (Figueroa et al., 2004; Sassman and Lee, 2005). Unlike in acidic conditions, TCs are not stable in alkaline conditions; yet they can form salts in both media (Halling-Sorensen et al., 2002). Therefore, according to their ionization patterns, it can be assumed that under environmental pH values (pH 4–8), the dominant form of TCs antibiotics would be the zwitterionic species and would reach the maximum concentration at pH 5.5.

Another reason for the observed higher sorption of TCs to soils is their ability to form complexes with chelating agents such as divalent metal ions and b-diketones and strongly bind to proteins (Oka et al., 2000). Although TCs are sparingly soluble in water (Florence and Attwood, 1981), the solubility of the equivalent hydrochlorides is more likely to be much higher (Thiele-Bruhn, 2003). However, in a soil column study, the presence of dissolved organic matter (DOM) in liquid manure showed an increase in mobility for tetracycline antibiotics (Aga et al., 2003). Similarly, other field studies indicated that the preferential flow caused by dry cracks and worm channels could enhance the movement of antibiotics to the tile drains (Kay et al., 2004). Moreover, the reported apparent distribution coefficients (K_d) between lagoon water and sediment for sulfamethazine and oxytetracycline were 8.3 and 351 L kg^{-1}, respectively. The K_d value of oxytetracycline was somewhat greater than the reported K d values of 77.6 L kg^{-1} in swine manure (Watanabe et al., 2008). Compared to the K_d values in soils or soil constituents, K_d of sulfamethazine is greater than the reported range (0.6-3.1 L kg^{-1}), and the K_d of oxytetracycline is within the reported range (0.3-3020 L kg^{-1}). The K_d value can vary depending on the properties of the sorbent and aqueous phase. In the lagoon water-sediment system, where pH is often near or above pK_a of tetracyclines and sulfonamides, zwitterionic or anionic species are dominant for tetracyclines, and neutral and anionic species are dominant for sulfonamides, which will result in a decrease of the K_d values.

2.3.3 Environmental implications

First, the habitual presence of antibiotics in environmentally relevant concentrations has been connected to chronic toxicity and the prevalence of resistance to antibiotics in bacterial species (Schwartz et al., 2006; Kummerer, 2009). In environmentally relevant concentrations, Thomulka and McGee (1993) reported that some of the tested antibiotics such as novobiocin, tetracycline, chloramphenicol, nalidixic acid, ampicillin, streptomycin were found to have a long term toxic effect on the reproduction process of *Vibrio harveyi*. Likewise, Froehner et al. (2000) reported matching behavior of the antibiotics chloramphenicol, nalidixic acid and streptomycin. Furthermore, the observed chronic effect was pronounced in the case of testing for many of the high volume antibiotics used for veterinary purposes and in aquaculture (Backhaus and

Grimme, 1999). Furthermore, different organisms like the freshwater flea, *Daphnia magna*, and the crustacean, *Artemia salina*, are found to be sensitive to the presence of antibiotics (Macri et al., 1988; Wollenberger et al., 2000). An acute toxicity test for some aquatic organisms revealed that the freshwater flea (*D. magna*) is the most susceptible among other tested organisms to sulfonamides antibiotics such as sulfamethoxazole, sulfachloropyridazine, sulfathiazole, sulfamethazine, sulfadimethoxine.

The permanent occurrence of antibiotics in many environmental compartments has contributed to the development of antibiotic resistance genes and bacteria. As a result, this limits the therapeutic potential of these antibiotics against human and animal pathogens (Kemper, 2008). Eventually, the concerns could be distressing since the bacteria present in the aquatic environment may be exposed to antibiotic residues on a regular basis (Rosal et al., 2010). The presence of antibiotics above a certain concentration creates selection pressure that eventually plays a significant role in the development and evolution of resistant bacteria. Thus, prolonged exposure and low environmental concentrations can account for the transfer of resistance genes into the ecosystem (Kummerer, 2004).

Increasing antibiotic resistance can occur through bacterial conjugation and transposition of transposable elements both in the same species as well as among members belonging to taxonomically unrelated species (Han et al., 2003). Direct toxic effects on exposed biota and ecosystem can also occur. Therefore, in WWTP, particularly in the biological process, the continuous exposure of bacteria to environmentally relevant concentrations of antibiotics is potentially considered as an appropriate setting for the development and spreading of resistance. Thus, more research is needed to better evaluate the role of wastewater treatment systems in the development of antibiotic resistance.

Due to the extensive use of antibiotics at sub-therapeutical doses for promoting growth and feed efficiencies in animal farms, the prevalence of bacterial resistance in soil is widely observed (Tueber, 2001). The effect of antibiotics on the soil microbial biomass has been documented (Kotzerke et al., 2008 and Thiel-Bruhn and Beck, 2005). More specifically, some changes in the physiological profile of soil microorganisms were observed in soil contaminated with sulfachloropyridazine, thus, increasing the resistance by the further addition of antibiotics is also observed. Additionally, the author concluded that due to the lower toxic concentrations compared to other organic contaminants, antibiotics pose a risk to soil microbial communities which indicates their ecotoxic relevance in the environment (Thiel-Bruhn, 2005). In this context, Gutierrez et al. (2010) reported that functions and structural diversity of soil microbial populations has been altered by the presence of sulfonamid antibiotics in soil even at relatively low concentrations. Further, a considerable increase of resistant genes were observed in soils previously treated with manure containing sulfadiazine, indicating that repeated applications of manure contributes to the abundance of sulfonamid resistant genes in soil (Heuer et al., 2011).

In the case of tetracycline antibiotics, Chee Sanford et al. (2001) reported that the existence and diversity of tetracycline resistant genes in lagoons and groundwater under two swine farms in US can be transported to humans and animals through drinking water and food chains subsequently, reducing the therapeutic efficiency of antibiotic treatments. The possibility of transfer of antibacterial resistance from agriculture to humans has been reported (Rhodes et al., 2000, Bogaard et al., 2000; Sengelov, 2003 and Gullberg et al., 2012). The transfer of resistant bacteria occurs by three pathways; food contamination, animal handling and manure application. For example, a study in grocery stores surveyed in Louisiana indicated that meat is widely infected by resistant bacteria and five out of 90 samples of retail pork were found to contain methicillin-resistance *Staphylococcus aureus* or MRSA (Pu et al., 2008). The same scenario was repeated in Washington D.C. suggesting that hog farms are a potential source for spreading a deadly new strain of MRSA (ST398). Furthermore, workers in CFCOs can be exposed to resistant bacteria by handling animals, feed and manure. They can also act as a source to other individuals. Third, the spread of manure in soil can be a rich environment for inducing bacterial mutations. Evidence of the presence of antibiotics in 48% of US streams was observed, of which 50 % of the tested streams were located downstream of agricultural areas (Koplin et al., 2002).

On the other hand, a study by Boxall et al. (2006) highlights the risk of transporting antibiotics in plants. They concluded that the potential for the uptake of veterinary antibiotics can be increased due to the prolonged exposure to these compounds in soils previously treated with contaminated manure. Similarly, a number of studies indicated that crops have the ability to uptake antibiotics such as fluoroquinolones and sulfonamides from soil (Migliore et al., 1998; Migliore et al., 2003 and Forni et al., 2002). In terms of the contributions of human activities to the development of resistant bacterial strains, Auerbach et al. (2007) indicated that more investigations are needed to fully understand this complex relationship.

It is evident that microbial degradation is playing an essential role in the breakdown of most soil-applied pesticides (Soulas and Lagacherie, 2001). Since antibiotics are designed to negatively affect microorganisms, their potential effect on the persistence of soil-applied pesticides should be investigated. Moreover, Kim et al. (2010) investigated the role of ionophore antibiotics in the degradation rate of the herbicide atrazine and found that an increase in the half-life for atrazine was observed in soil in the presence of applied antibiotics suggesting an inhibitory effect of the soil micro-organisms responsible for atrazine degradation in soil. To control the role of antibiotics in such a process, given the variety of environmental factors, can be unpredictable. Therefore, there is a need to find an approach to assess the impact by which veterinary antibiotics affect pesticide degradation in soil.

2.3.4 Antibiotics of interest

Oxytetracycline

Oxytetracycline (OTC) belongs to the tetracycline group of antibiotics. The chemical structure is shown in Figure 2.3 (a). In the EU, OTC accounts for 66% of the total veterinary antibiotics used; this was approximately 2294 tons in 1997 (Boatman, 1998). While in US farms, about 9200 tons were used in 2003, of which 3000 tons were tetracyclines (A.H.I., 2005).

OTC antibiotics have bacteriostatic effects and a wide spectrum of activity, and have been used in the treatment of a large number of infections caused by susceptible organisms (Injac et al., 2008). In urine and faeces, 40-80% of the quantity excreted is as parent compound; it has been measured in a pig slurry up to 410 $\mu g\ L^{-1}$ (Campagnolo et al, 2002). However, OTC concentrations in soil have been measured up to 10 $\mu g\ L^{-1}$ in soil (Hamscher et al., 2000). OTC is the preferred tetracycline antibiotic for aquaculture. Due to the lack of further treatments to the effluents of fish ponds, the contamination of a wide range of water systems by OTC residues is likely (Himmelsbach and Buchberger, 2005).

In fields, which had been previously sprayed with manure slurry, OTC was detected at concentrations of 9 $\mu g\ kg^{-1}$ in the upper 10 cm of the soil samples after two days of manure application (Hamscher et al., 2000). The degradation of OTC in soil has been promoted by increasing the moisture content from 60 to 100%. However, OTC becomes persistent in water-saturated manure (Wang and Yates, 2008). The calculated half-life of OTC in manure-amended soil (amendment ratio 5%) was 33 days while, in non-amended soil at moisture contents of 20%, the half-life was 56 days. This indicates that OTC may become persistent in the environment after it is released from manure applied to soil. Studies have also shown that OTC can persist in the sediment for several months (Bjorklund et al., 1990; Hektoen et al., 1995). The increase in temperature appreciably accelerated OTC degradation, and a significant thermal degradation at high temperatures around 35 ºC in manure was observed. Furthermore, the OTC half-life was determined to be 8.1 days in manure at 25 ºC with a moisture content of 80%. No obvious effect of the coexistence of the antibiotics tetracycline, sulfadimethoxine, or penicillin G was observed on OTC degradation in manure.

Monensin

Monensin is an antibiotic in the ionophore family; they comprise a class of antibiotics exclusively used for veterinary purposes. When the monensin molecule is ionized, the carboxylic group becomes charged; in order for it to be neutralized, hydrogen bonding between the molecule and monovalent cations are formed resulting in a complex. This zwetterionic structure provides the molecule with an extra hydrophobic exterior (Gertenbach and Popo, 1975). This chelation potential allows monensin to disrupt the ion gradient of the cell membrane of microorganisms causing cell scrambling and shrinking and ultimately leading to cell death (Shen and Brodbelt, 2000; Lopes et al., 2002; Kiehl et al., 1998). The chemical structure is shown in Figure 2.3 (b). In the US, monensin is the only feed additive permitted for use in lactating cows. The use of monensin for increasing milk production was approved by the US Food and Drug Administration in November 2004 (Federal Register, 2004).

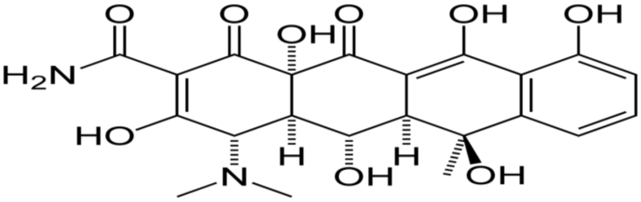
When monensin is released into the environment, it has the potential to persist and reach aquifers. However, the reported biodegradation rates indicate that rapid biological attenuation is possible. The half-lives range from less than 2 days (Sassman and Lee, 2007) to 13.5 days (Carlson and Mabury, 2006). The reported distribution coefficient (K_d) ranges from 0.915 to 78.6 (L kg^{-1}) for different types of soils (Sassman and Lee, 2007). Monensin concentration was found to be 2000 µg kg^{-1} in the fraction of suspended solids. Monensin concentrations are detected in surface water as high as 1.2 µg L^{-1} and up to 30 µg L^{-1} in sediments near agricultural regions. Monensin is reported to be immobile in the soil (Carlson and Murray, 2006; Donoho, 1984). Furthermore, monensin persists at relatively high concentrations in manure transport and storage systems. Being hydrophobic, monensin is expected to strongly sorb to sediments, reducing the likelihood of moving down the soil profile. On the other hand, monensin concentrations from of 1 to 10 µg L^{-1} were detected in flush lane water samples and in lagoon water samples. Additionally, monensin was detected in ground water samples within the production facility of dairy farms. However, no evidence of the presence of monensin was observed in ground water underneath fields that receive lagoon manure water **(**Watanabe et al., 2008**).**

Sulfachloropyridazine

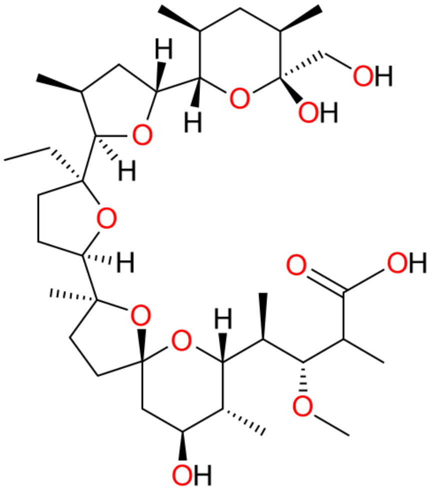
Sulfonamides are synthetic antimicrobial agents with a broad spectrum against most gram-positive and gram-negative bacteria. Sulfachloropyridazine is a member of the antimicrobial class of sulfonamides; they represent 2.3% of all antibiotics used in the United States and 21% of total antibiotics sales in the United Kingdom (Sarmah et al., 2006). Fundamentally, sulfonamides are designed to disturb the bacterial synthesis of folic acid, which is vital for the synthesis of bacterial DNA. They have a bacteriostatic effect that allows them to suppress bacterial growth. The chemical structure is shown in Figure 2.3 (c). According to Thiele- Bruhn et al. (2004), up to 90% of sulfonamides are excreted by animals after consumption.

In terms of occurrence in several constituents, SCP has been detected, notably, in soil at concentrations of 1.55 mg kg^{-1} (Boxall et al., 2002) and up to 365 mg kg^{-1} (Kay et al., 2005). However, in manure, it has been detected at concentrations of 91 mg kg $^{-1}$ (Martinez-Carballo et al., 2007). Further, SCP was detected in soil at concentrations up to 365 mg kg^{-1} (Key et al., 2004).

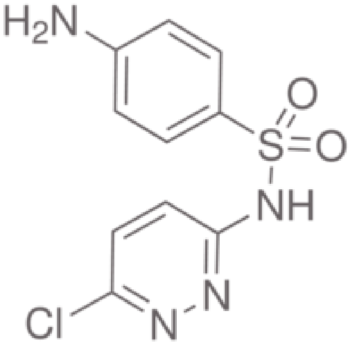
The sulfanomide distribution coefficient (K_d) in soil has been found to range from 0.9 to 3.5 indicating their high mobility under field conditions (Boxall et al., 2002). Further, Thiele-Bruhn et al. (2005) showed that soil pH and the properties of soil organic colloids are important factors in determining the extent of sulfonamides sorption on soil. It is evident that SCP is capable of inducing changes in soil microbial community; Gutierrez et al. (2010) indicated that sulfanomides can adversely affect the soil microbial population at relatively low concentrations. Similarly, Heuer et al. (2011) reported that repeated manure applications increased the number of sulfanomide resistant genes (at low concentrations) in soil.



(a)



(b)



(c)

Figure 2.3 Chemical structure of (a) Oxytetracycline (Loke et al. 2002), (b) Monensin (Sassman and Lee, 2006) and (c) Sulphachloropyridazine (Terlaak et al., 2006)

2.4 Pesticides

Non-point source are the primary pathway for pesticide pollution which is often the cause of water quality impairment. The presence of pesticides in waste water are from different sources such as disposal sites and landfills where industrial or agricultural waste are burnt without treatment, as well as discharges from industrial effluents and from pesticide production plants. Further, spray drift, surface runoff, and field drainage are relevant routes of exposure; therefore, contamination via groundwater discharge may occur. In the U.S., about 2.2 billion kilograms of pesticides are used annually, with agricultural usage accounting for 77% (Kiely et al., 2004); of which herbicides, as the most common group, accounts for 65% from the total amount applied. In the United States, over 273 million kilograms of pesticides enter the environment every year (Stevenson et al., 2003). In US, 68,000 wells in 45 states have been tested of which, 16,000 wells in 42 states were found to contain pesticides. Approximately 10,000 of these wells contained pesticide concentrations which exceeded EPA drinking water standards (EDS, 2000). Thereby, it is not surprising that some herbicides residues have been detected in the atmosphere. Furthermore, atrazine and alachlor have exceeded the allowable level in drinking water in the US (USGS, 1995). Moreover, about 46 different pesticides had been detected in ground water and 76 pesticides in surface water bodies (USEPA, 1998). Triazines herbicides are relatively mobile and have been detected in several public and domestic surface and ground water resources at concentrations higher than drinking water guidelines (Trotter et al., 1990; Pauli et al., 1990).

The occurrence and fate of pesticides in natural environment is complex and continuously influenced by transport, sorption, leaching and degradation. Each process depends on the physico-chemical properties of pesticides, soil type and the bioavailability. Pesticides sorption has been linked to the amount of organic matter OM in soil, the higher the amount of OM, the more binding sites available in soil. Apparently, hydrophobic pesticides have a strong tendency to bind with the OM sites compared to the hydrophilic ones. Owing to the strong negative charge of the organic matter, cationic herbicides are attracted. This could in turn limit the pesticide availability to control weeds (Bhandari et al., 2009).

Leaching is expressed by the weak tendency to bind with soil which eventually leads to the downward movement into soil profile. This process is governed by the pesticide solubility, the degree of soil permeability, site texture, soil pH and rainfall. Therefore, pesticides in high permeable soil can readily move down to reach ground water. The presence of animals such as earth worm can increase the pore size due to constructing channels; thus enhancing the leaching potential as well (Buttler et al., 2003). The degree of sorption of organic contaminants to sediment has a major influence on its transport and fate in the environment (Chiou et al., 1998) and the risk of leaching and the extent of contamination of chemicals into groundwater or to surface waters (TerLaak et al., 2006).

The degradation of pesticides can be abiotic as a result of volatilization, photolysis and hydrolysis. However, it was reported that abiotic transformation is dominantly by hydrolysis and redox reactions. Since pesticides are continuously exposed to saturated environment, pesticide molecule can be cleaved into smaller water soluble portions by hydrolysis. The degree of this process depends on the functional groups attached to each molecule. For example, carboxylic acid esters, organophosphate esters, amides, anilides, triazines and carbamates are susceptible to breakdown by hydrolysis. Potentially, microorganisms play important role in the biodegradation of pesticides due to the release of the necessary enzymes to mineralize complex organic compounds. Therefore, various species of bacteria and fungi can degrade herbicides. The transformation products (metabolites) formed after degradation could be persistent in the environment or can be more toxic than the parent compounds.

Due to the degree of resistance of many pesticides to breakdown during the wastewater treatment processes, these compounds can enter into the aquatic environment. Miltner et al. (1989) indicated that herbicides such as, atrazine, metolachlor, metribuzin, simazine and carbofuran have been detected from the influents of three water treatment plants in US. Therefore, great measures have been taken to develop new treatment to completely remove the residues of pesticides in drinking water as suggested by the Food Quality Protection Act (FQPA) of 1996 which regulates the risks caused by pesticides to human beings from all the anticipated dietary exposures. It was estimated that 0.1% of the applied pesticides reach the target; thus significant amount is expected to be released to the environment. Furthermore, evidence of adverse effects on non-target organisms has been reported (Pimentel and Levitan, 1986). In this study the focus will be given to the triazine herbicides due to their wide usage in agriculture for weeds control in a wide variety of crops.

Metribuzin

Metribuzin *(4-amino-6-tert-butyl-4, 5-dihydro-3-methyltio-1, 2, 4-triazin-5-one*) is a triazine herbicide, which inhibits the photosynthesis in susceptible plant species. The chemical structure is shown in Figure 2.4. Usually, it is used to control annual grasses and broadleaf weeds in field and vegetable crops, in turf grass and on fallow lands (Kidd et al., 1991).

Metribuzin exhibits a moderate persistence in the soil. Webster (1976) found that metribuzin persisted in soil in the year following application with estimated half-life of 60-90 days in several types of soils. Further, metribuzin is characterized by its high water solubility, adsorption capacity to the soil ($K_{oc} = 60$), and it is low affinity to most soils, which therefore, enhance the likelihood of its leaching potential to ground water (Wauchope et al., 1992). The rate of which a herbicide degrades is in part a function of its molecular structure, chemical and microbial properties of the soil as well as the climatic conditions (Allen, 1986). The USEPA lifetime health advisory level for metribuzin in drinking water is 200 $\mu g\ L^{-1}$ (Selim, 2003).

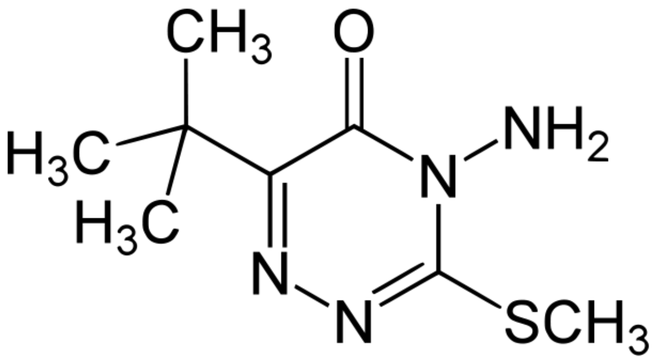


Figure 2.4 Chemical structure of metribuzin (Maqueda et al., 2009)

Connecting Text to Chapter 3

Manure is applied for fertilization as a common practice in agriculture. Since manure contains a lot of antibiotics, they could potentially contaminate agricultural soils and eventually contaminate groundwater supplies. As wastewater is used for irrigation in many semi-arid and arid areas, this could introduce surfactants to the soil as well.

Due to lack of information concerning the effect of non-ionic surfactants, when they coexist with antibiotics in soils, the study in Chapter 3 was undertaken. In this chapter, we address the fate and transport of the antibiotic oxytetracycline in the presence of a non-ionic surfactant Brij 35 in irrigation water. While a field study was carried out using lysimeters to assess the fate and transport of antibiotics in soil, a sorption experiment was conducted in the laboratory to provide a solid basis for interpreting the results obtained from the field study.

This chapter was published as a research publication in the journal of Environmental Management in 2013, vol. 116: 125-134. The manuscript is co-authored by my supervisor Dr. S. O. Prasher, and Dr. Ramanbhai Patel, a research associate in the department. The format of the original draft has been modified to remain consistent with the thesis format. All literature cited in this chapter is listed in the Bibliography (Chapter 9) at the end of the thesis.

Chapter 3 - EFFECT OF NONIONIC SURFACTANT BRIJ 35 ON THE FATE AND TRANSPORT OF OXYTETRACYCLINE ANTIBIOTIC IN SOIL

Eman ElSayed, Shiv Prasher and Ramanbhai Patel

Abstract

In many parts of the world, river water is used for irrigation. Treated, partially treated, and even untreated water from waste water treatment plants is discharged directly into rivers, thereby degrading the quality of the water. Consequently, irrigation water may contain surfactants which may affect the fate and transport of chemicals such as pesticides and antibiotics in agricultural soils. A field lysimeter study was undertaken to investigate the effect of the nonionic surfactant, Brij 35, on the fate and transport of an antibiotic, Oxytetracycline, commonly used in cattle farms. Nine PVC lysimeters, 1.0 m long x 0.45 m diameter, were packed with a sandy soil to a bulk density of 1.35 Mg m^{-3}. Cattle manure, containing Oxytetracycline, was applied at the surface of the lysimeters at the recommended rate of 10 t/ha. Each of three aqueous Brij 35 solutions, 0, 0.5 and 5 g L^{-1} (i.e., 'good,' 'poor' and 'very poor' quality irrigation water) were each applied to the lysimeters in triplicate. Over a 90 day period, soil and leachate samples were collected and analyzed. Batch experiment results showed that the presence of the nonionic surfactant Brij 35 significantly reduced the sorption coefficient of OTC from 23.55 mL g^{-1} in the aqueous medium to 19.49, 12.49 and 14.53 in the presence of Brij 35 at concentrations of 0.25, 2.5 and 5 g L^{-1}, respectively. Lysimeter results indicated the significant downward movement of OTC at depths of 60 cm into soil profile and leachate in the presence of surfactant. Thus, the reuse of waste water containing surfactants might enhance the mobility of contaminants and increase ground water pollution.

Keywords: Nonionic Surfactants, Brij 35, Oxytetracycline, Antibiotic, wastewater, fate, Lysimeter

3.1 Introduction

Given the scarcity of water in many parts of the world, the reuse of wastewater has become an important alternative option for irrigation. In developing countries, sometimes wastewater is used to irrigate crops and vegetables; this wastewater may be untreated, or partially treated, or both. Chatterjee (2008) indicated that 85% of 53 cities in developing countries discharge untreated or primary treated wastewater to irrigate land in order to keep pace with the ever increasing demand for food resulting from a growing population. As a consequence of this practice, there may be an increase in bacterial infections, as well as roundworm and diarrheal diseases. A recent survey indicates that 46 countries representing 75% of the world's irrigated land make use of polluted water for irrigation (Drechsel et al., 2010). Globally, Hamilton et al. (2007) estimated that approximately 20 million hectares of land are irrigated with wastewater, and this area is expected to markedly increase in the next few years.

Wastewater is a mixture of inorganic and organic substances originating in the discharge of municipal and industrial effluents. Many studies reveal that surfactants have been detected as the highest concentrations found among the organic chemicals in wastewater and sludge (Brunner et al., 1988; Field et al., 1992; Wild et al., 1990). Non-ionic surfactants concentrations ranging from 10^2-10^3 mg L^{-1} have been detected in wastewater (Narkis and Ben-David 1985). Such nonionic surfactants as alcohol ethoxylates (AEO) and alkylphenol ethoxylate (APEO) are being used extensively to remove skin grease in the leather industry. Nonionic surfactants were the major pollutants in untreated wastewater samples from the textile industries (Castillo et al., 1999). Although the treatment of effluent in wastewater treatment plants (WWTP) eliminates the surfactants which undergo degradation to metabolites such as nonylphenol ethoxylates (NPEOs), Loyo-Rosales et al. (2007) found that WWTP do not remove all of the metabolites. Therefore, many household products contribute to an abundance of these contaminants in urban sewers (Conn et al., 2006; Loyo-Rosales et al., 2007; Stuart et al., 2012).

Basically, non-ionic surfactants do not ionize in water because they have a non-dissociable hydrophilic group (*e.g*., alcohol, phenol, ether, ester, or amide) and are considered to be amphiphilic compounds. Generally, the presence of nonionic surfactants in irrigation water leads to two major concerns. First, nonionic surfactant byproducts such as NPEO and nonylphenol (NP) are estrogen disrupting compounds. This may result in changes in the sex ratio, a decrease in fish population and increase in malformations have been observed in animals (Esperanza et al, 2004). Additionally, Barber et al. (2009) indicated that nonionic surfactant degradation products NP were detected in wells in the US; in the United States, potable water contamination is of great concern due to the estrogenic effect of these compounds with the continuous disposal of wastewater treatment plant effluent. Therefore, alcohol ethoxylates (AEs) are now used as an alternative to NPEOs, as they are safer in terms of their rapid degradation to less toxic, less persistent and less estrogenic metabolites. Secondly, nonionic surfactants in irrigation water may have an impact on the mobility of chemicals in soils and result in the contamination of groundwater (Huggenberger et al., 1973; Kan and Tomson, 1990; Aronstein et al., 1991; Rodriguez-Cruz et al., 2004). For example, nonionic surfactants at low concentrations (0.04 g kg^{-1}) decreased the mobility of the herbicide metolachlor in soil; however, at high concentrations (5-50 g kg^{-1}) the mobility increased (Sanchez-Camazano et al., 1995). Furthermore, Katagi (2008) reported that the mobility of pesticides is increased in leached water when there are high concentrations of surfactants. Generally, nonionic surfactants increased the downward movement of pesticides in soil whereas cationic surfactants markedly decreased the mobility of pesticides in the soil. Nilufer (2005) stated that at low concentrations (12 mg L^{-1}) of LAS and NP, there is no effect on the mobility of such herbicides as atrazin, metalochlor and metribuzin. However, Tao et al. (2006) indicated that at low concentrations 0-20 mg L^{-1}, surfactants have the potential to decrease sorption and mobilize herbicides such as atrazin.

Agricultural effluents are known as a main, non-point source for pollution with pharmaceutically active compounds (PhACs) and their metabolites. Pharmaceutical antibiotics are widely used in agriculture not only to control disease but also as a growth promoter in the livestock industry (Thiele-Bruhn, 2003). Application of manure from such industries on agricultural land is of great concern (Stuart et al., 2012). Recent studies revealed that manure may contain as much as 60-90% of the antibiotics excreted in animal feces in the active form due to its poor metabolism. As a consequence, the inactive antibiotic conjugates could be bioactive in manure by cleaving the acetyl group, resulting in the release of the original active form. They can be more persistent in the environment due to their high polarity. Martinez-Carballo at al., (2007) reported that oxytetracycline (OTC) has been detected in manure in concentrations as high as 29 µg g^{-1}. Similarly, Uslu and Balcioglu (2009) found tetracyclines in manure samples around a concentration of 46 µg g^{-1}. Antibiotics may enter the environment via different pathways such as agricultural soil, ground and surface water (Halling-Sorensen et al., 1998). OTC is considered the preferred tetracycline antibiotic in fish farms and as an animal feed additive; given that fish farm effluent lacks additional treatments to reduce OTC residue, OTC residues could be introduced into water bodies easily as a result of the discharge from fish farms (Himmelshbach and Buchberger, 2005). The sorption coefficient (Kd) values of OTC are found to be between 416 and 1026 L/kg in sandy and sandy loam soil, respectively (Rabolle and Spliid, 2000). Sorption of OTC to clay loam and loam sand soil was tested as a function of pH and ionic strength and the results show that as pH and ionic strength increase, the sorption decreases (Terlaak et al., 2006). Similarly, as dissolved organic matter (DOM) increases, OTC sorption decreases leading to increasing mobility; this suggests that DOM is an important factor affecting OTC leaching in soil (Kulsherstha et al., 2004).

Terlaak et al. (2006) stated that manure contains high amounts of ammonium nitrate which is transformed to nitrate by releasing protons, and as a result, it decreases soil pH. Therefore, antibiotics adsorption potential onto soil varies considerably after manure application and the chemical interaction of manure with the soil. Additionally, Wang and Yates (2008) estimated the half-life of OTC to be 33 days in manure-amended soil compared to 8.1 and 56 days in manure and non-amended soil, respectively; suggesting that OTC persistence in soil may increase after manure application to soil. Furthermore, the half-life of OTC in soil under aerobic conditions ranged between 26-56 days in non-sterile soil, whereas the half-life increased to 99-120 days in sterile soils. This confirms the fact that microorganisms can degrade OTC. Nevertheless, abiotic degradation is important in the dissipation process in soil (Yang et al., 2009). Blackwell et al. (2009) investigated the fate of OTC in a sandy loam soil column under extreme rainfall conditions and found that OTC was detected in soil samples only from the 0-5 cm top of the lysimeter profile; OTC was not found in the leachate due to the high sorption coefficient and its persistence in soil. Similar results were obtained by Rabolle and Spliid (2000) and Blackwell and Boxall (2007). However, Hamscher et al. (2000) analyzed the leachate samples collected from agricultural land and reported that chlortetracycline, oxytetracycline, tetracycline and tylosin were detected at concentrations ranging from 0.1 to 0.3 μg L^{-1}. This could pose a risk of ground water contamination and bacterial resistance. On the other hand, Boxall et al. (2006) reported that OTC significantly reduced plant growth and similar effects have been documented with other groups of pharmaceuticals as well. Antibiotics are also considered as emerging contaminants; they are of great concern because of their potential to enhance the rise of antibiotic resistant genes. A prolonged exposure to low doses of antibiotics may lead to an increase in drug resistance among the soil microbial community. Moreover, Rhodes et al. (2000) found evidence of the likelihood of the transfer of antibacterial resistance to humans.

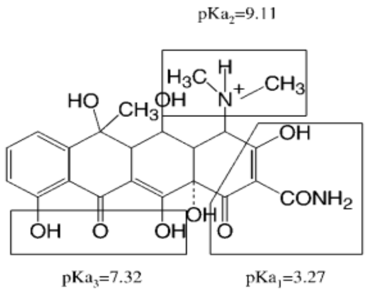
From the literature, it is evident that when manure containing oxytetracycline is applied to agricultural land, oxytetracycline may enter the water system and then surfactants may affect its mobility. To the best of the authors’ knowledge, no study has been done to address the fate of oxytetracycline when it coexists with the nonionic surfactants in soil. Therefore, this study was conducted to investigate the mobility of oxytetracycline in soil (with low organic matter content) and water in the presence of nonionic surfactant Brij 35 in the irrigation water.

3.2 Materials and methods

3.2.1 Study compounds

Oxytetracycline hydrochloride (OTC) 95% HPLC grade from Sigma-Aldrich, solubility 1 g L^{-1} (Table 3.1) and Oxyvet as a commercial grade of OTC used in cattle farms were purchased from CMFO company, Quebec. Demeclocycline (DMCTC) was used as an internal standard (to better estimate the loss of OTC during extraction procedure from soil and leachate samples) and it was purchased from Sigma-Aldrich. A pure standard (Pestanal®) and formulation (Sencor 75) of metribuzin were purchased from Sigma-Aldrich. The non-ionic surfactant Brij 35 [Polyoxyethylene lauryl ether $(C_2H_4O)_{23}$-$C_{12}H_{25}OH$] with critical micellar concentration (CMC) = 74 mg L^{-1} and Log P is approximately 3.13 (HERA, 2009). HPLC-grade methanol and acetonitrile were obtained from Sigma-Aldrich. Mobile phase chemicals were purchased from Fisher Scientific. Double–deionized water (Milli-Q, Millipore, Molsheim, France) was used in the preparation of standard solutions and mobile phase solutions.

Table 3.1-Physical and chemical characteristics of Oxytetracycline

Physical - chemical properties	Chemical structure
Solubility : 1 g/L MW : 460.44 Log K_{ow} : -1.22[a] GUS index : -0.91[b] Pka1 : 3.27 [c] Pka2 : 7.32 pKa3 : 9.11	

[a] Loke et al. (2002) [b] PPDB (2009) [c] Sassman and Lee (2005)

3.2.2 Soil Characteristics

Belonging to the St. Amable complex, the sandy soil used was obtained from a field in the Macdonald Campus of McGill University, Ste-Anne-De-Bellevue, Qc. Physical and chemical properties of the soil are given in Table 3.2.

Table 3.2-Physical and Chemical Characteristics of Soil

Soil Type	Sand (%)	Silt (%)	pH	Bulk Density (Mg m^{-3})	Organic Matter (%)	CEC (cmol kg^{-1})	Hydraulic Conductivity (cm d^{-1})	Zero point of charge (zpc)
Sandy	92.2	4.3	5.5	1.35	2.97	4.9	1.67 (*S.D. = 0.45)	3.4

* S.D. stands for standard deviation

3.2.2.1. Batch adsorption experiment

Adsorption of OTC onto soil in the presence of the nonionic surfactant Brij 35 was investigated through a soil equilibrium technique. Triplicate soil samples (1 g) were equilibrated with an aqueous solution (20 mL) of OTC at concentrations ranging from 5 to 50 µg mL^{-1} in factorial combination with Brij 35 concentrations of 0, 0.02, 0.25, 0.5 and 5 g L^{-1}. All solutions contained 0.01 M $CaCl_2$ to mimic the ionic strength of groundwater (Wilde et al., 2008). The soil slurry was placed in a 50 mL centrifuge tube, and placed on a shaker, for 48 hrs. The slurry was centrifuged at 2683 g for 20 min. Extraction and analysis of OTC proceeded, as described above. The proportion of OTC adsorbed was calculated by taking the difference between the amount initially present in solution and the amount remaining in solution after equilibrium with the soil.

3.2.2.2. Analytical procedure

The soil samples and leachate were analyzed by HPLC with diode array detection DAD using eclipse plus C18 column (4.6 x 150 mm) from Agilant, USA. The mobile phase was 15% acetonitril and 85% of water containing phosphate buffer at pH 2.5. The flow rate was 1 mL min^{-1} and detection wavelength was at 355 nm for OTC and 254 nm for DMCTC with detection limit of 0.1 ng g^{-1}.

OTC sorption data were fitted to the freundlich adsorption isotherm equation:

$$q = K_F \, C_{aq}^{n} \qquad \text{Eq. 3.1}$$

Where

q is the amount of OTC sorbed (μg g^{-1}),

C_{aq} is OTC concentration after equilibrium in μg mL^{-1}, and

K_F, n are the Freundlich affinity and nonlinearity coefficients, respectively (mL g^{-1})

Organic carbon normalized coefficient values for oxytetracycline in the absence of surfactant and in the presence of surfactant were obtained as follows:

$$K_{oc} = \frac{K_F}{f_{oc}} \qquad \text{Eq. 3.2}$$

Where

f_{oc} is the organic carbon fraction of the soil (0.0297 g g^{-1} for the soil used), and

K_{oc} is the partition coefficient of the contaminant in the organic fraction of the soil (mL g^{-1}).

3.2.3. Field experimental set up

The field experiment investigating oxytetracycline transport in a sandy agricultural soil was conducted in nine outdoor PVC lysimeters set up at the Macdonald Campus of McGill University, Ste-Anne-De-Bellevue, Quebec. The lysimeters (0.45 m O.D. × 1 m long), were sealed at the bottom to 0.6 m × 0.6 m PVC sheets. Each lysimeter was packed in layers with sandy soil and adjusted to a bulk density of 1.35 Mg m^{-3}. A 0.05 m diameter drainage pipe was installed at the bottom of each lysimeter. Four, 10 mm diameter, soil sampling holes were made in each lysimeter at depths of 0.1, 0.3 and 0.6 m the soil surface (Fig. 3.1). The lysimeters were sheltered to prevent the entry of natural precipitation.

3.2.3.1. Application of tested compounds

Antibiotic free manure was collected from a cattle farm in Ham-Sud, Quebec. The manure samples were mixed before adding the antibiotic. At the end of June 2009, before the start of the experiment, all of the lysimeters were irrigated, bringing them to saturation. The drainage pipe at the bottom of each lysimeter was left open throughout the study.

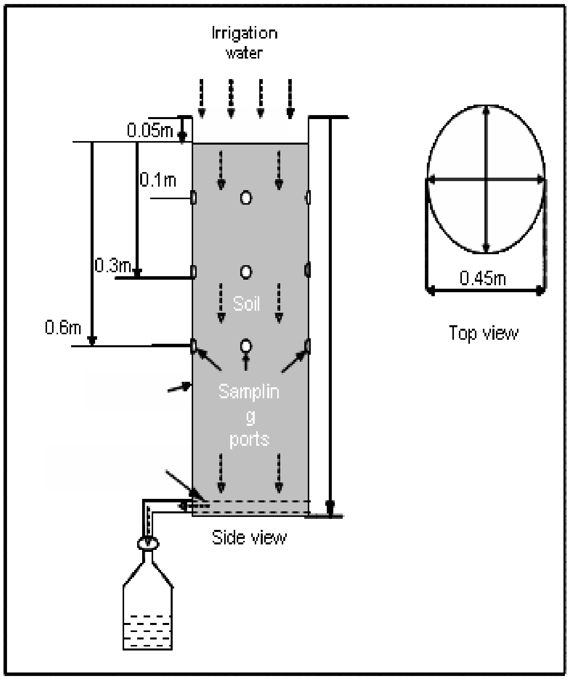


Figure 3.1 Schematic design of the lysimeter

The next day (Day 0), with the lysimeter's soil at field capacity**,** homogenized manure (10 Mg ha^{-1}) was applied to the surface of all of the lysimeters and manually mixed into the top 30 mm of soil (Chettri and Thapa, 2004) after being spiked with oxytetracycline in the form of Oxyvet according to the findings of Arikan et al. (2007). The spiked concentrations were calculated after adjusting the amount of OTC extracted from manure in Arikan’s study (115 µg g^{-1}) to the area of the lysimeter and the amount of manure applied. Metribuzin was then sprayed on each lysimeter’s soil surface (July 1, 2009) at the locally recommended rate for potatoes (1 kg a.i. ha^{-1}) as a common practice. Irrigation water (70 mm) , containing one of three different concentrations of Brij 35 (0, 0.5 or 5.0 g L^{-1}) was applied at day 0, day 21, day 42, day 63, according to the recommended irrigation practice for potatoes. Each treatment was replicated three times. While these surfactant concentrations may appear to be high concerning the environmental concentrations, Abu-Zreig et al. (1999) have studied the effect of surfactants on atrazine movement in soils using concentrations up to 10 g L^{-1}.

3.2.3.2. Soil and leachate sampling

Soil samples were collected at the surface as well as at depths of 0.1, 0.3 and 0.6 m, through 4 sampling ports in the side of the lysimeters. Soil samples were collected on 8 occasions: 0, 1, 5, 11, 22, 43, 60 and 90 days after the application of manure. For each surfactant concentration, three replicate soil samples (3 lysimeters) were taken at each of the four depths, and samples from a common treatment × depth were combined in a composite sample (~15 g). Subsamples of about 5 g were taken from each composite sample, and their moisture content determined. The remaining portions of the samples were stored in sealed bags in the freezer at -24ºC until extraction. Leachate samples (1 L) were collected as a subsample of a total of approximately 11 L of leachate collected at the outlet at the bottom of each lysimeter following each of the four irrigation events. The subsamples were then transported to the lab and immediately extracted to prevent any chance of OTC degradation.

3.2.3.3. Mass balance calculations

At each sampling date, the total antibiotics mass recovered from each lysimeter was calculated as the sum of the antibiotic recovered in soil samples across all depths of the soil profile. Adding the antibiotic mass in the leachate to that in the soil would total the initial antibiotic mass applied, minus any losses (unrecovered oxytetracycline) due to degradation or volatilization (Eq.3.3).

$$OTC_{init} = 1590.4\,\rho\left[C_{(0-5)}\theta_{(0-5)}\,h_{(0-5)} + C_{(5-15)}\theta_{(5-15)}h_{(5-15)} + C_{(15-45)}\theta_{(15-45)}h_{(15-45)} + C_{(45-70)}\theta_{(45-70)}h_{(45-70)}\right] + \left[C_{leach}V_{leach}\right] + OTC_{lost}$$

Eq. 3.3

Where

OTC_{init} Total oxytetracycline (mg) initially applied

OTC lost	Oxytetracycline lost through degradation, volatilization, etc. (mg)
ρ	Soil bulk density, (g cm^{-3})
$C_{(x-y)}\theta_{(x-y)}h_{(x-y)}$	Oxytetracycline concentration and soil moisture content, respectively, in soil layer h ranging from depth x to depth y (mg g^{-1}).
C_{leach}	Oxytetracycline concentration in leachate (mg L^{-1})
V_{leach}	Volume of leachate
1590.4	Soil layer surface area, $\pi\left(\frac{D}{2}\right)^2$, where D = 45 cm

In order to calculate the mass of oxytetracycline recovered in the soil layer samples, the following equation was used for this purpose

$$\text{Mass of OTC} = [C\ (m)] * \rho * a * h \qquad \text{Eq. 3.4}$$

Where

C = laboratory reported analytical oxytetracycline concentration in soil samples (mg g^{-1}),

m = moisture content of soil samples (mass water /mass dry soil mg g^{-1}),

ρ = soil bulk density (g cm^{-3}),

a = area of lysimeter (m^2) and

h = sampling depth of soil layers (cm).

3.2.4. Extraction from leachate and soil samples

3.2.4.1. Leachate samples extraction

Leachate was extracted right after it was transported from the lysimeters. Each 1 L subsample was filtered through 90 mm filter paper, followed by filtration through a 45 mm filter (Advantec, Japan), to remove coarse and fine suspended matter, prior to extraction. HLB cartridges from Oasis Co. Ltd, NY were used in the solid phase extraction (SPF). Prior to extraction, 2 g of EDTA were added to the sample followed by the addition of 100 µL of DMCTC. Preconditioning of each cartridge began by passing 5 mL of water through each cartridge twice, then 5 mL of 50:50 water: methanol (v/v), followed by 100 % methanol, all at a flow rate of 10 mL min^{-1}. The sample filtrate was then passed through the cartridges then washed twice with 5 mL of water, to elute OTC and DMCTC. Collected in a test tube, the 10 mL of eluate was evaporated under a N_2 stream, residue redissolved in 1 mL of acetonitrile, then passed through 0.22 µm syringe driven filter (Millex - GV, Japan), and the filtered solution was transferred to a vial for HPLC analysis.

3.2.4.2. Soil samples extraction

One gram of soil sample was weighed into 50 mL centrifuge tube and 5 mL of extraction buffer (0.1 M McIlvaine buffer (Na_2HPO_4 and citric acid at pH 7) / 0.1 M EDTA / methanol 25:25:50 v/v) then DMCTC were added. The tube was vortexed for 30 s and placed in an ultrasonic bath for 15 min. It was then centrifuged at 2683 g for 20 min. Supernatant was decanted and the extraction procedure was repeated twice. The combined supernatants were passed through a 45 mm filter paper, and then evaporated under a N_2 stream. Samples were re dissolved in 1 mL of acetonitrile and passed through a 0.22 µm syringe driven filter prior to HPLC analysis.

3.2.5. Data analysis

A statistical model using repeated measures over time and depth was employed to determine if the oxytetracycline concentrations differed between treatments, over time and with varying depths. Data was analyzed with PROC MIXED in SAS v. 9.2 (SAS Institute Inc., 2010).

3.3 Results and Discussion

3.3.1. OTC adsorption in the presence of Brij 35

Adsorption plays an important role in the many factors affecting the transport of chemicals in soil. To the best of the author's knowledge, no study has been conducted to investigate the sorption behavior of OTC in the presence of nonionic surfactant Brij 35. Therefore, the sorption experiment in the presence and absence of Brij 35 was carried out; the results demonstrate that the amount of OTC sorbed was higher in the absence of Brij 35; however, it decreased in the presence of surfactant at concentrations above CMC.

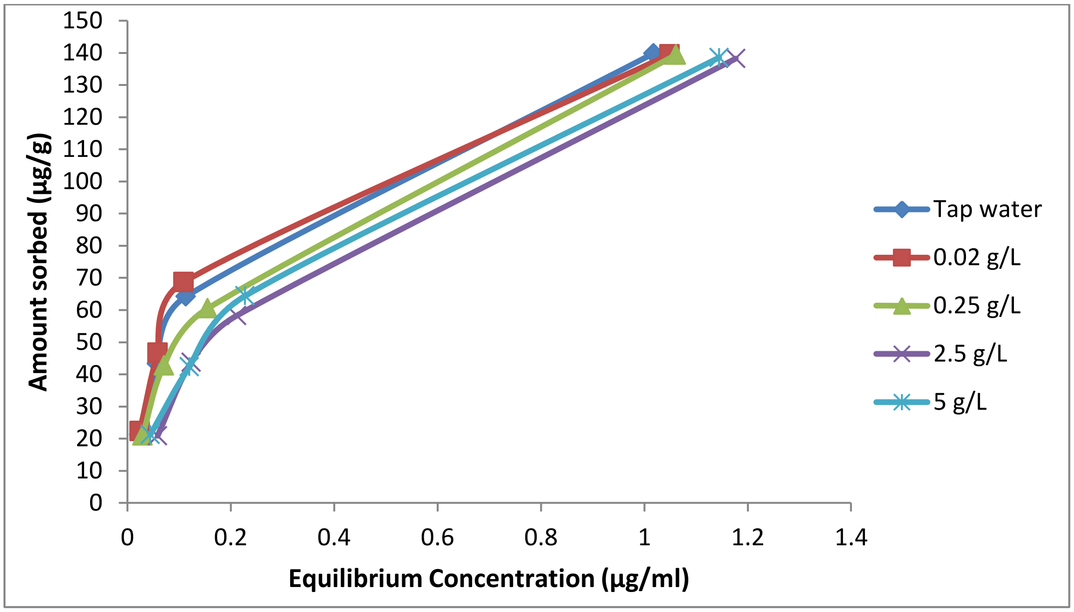


Figure 3.2 Oxytetracycline isotherms in the absence and presence of the non-ionic surfactant Brij 35

Fig.3.2 shows the sorption isotherms of OTC in Bij35 solutions at concentrations (0, 0.02, 0.25, 2.5 and 5 g L^{-1}). All isotherms obtained for OTC fit well the freundlich model Eq. (3.1), with R^2 values between 0.93 and 0.98. At low concentrations, sorption tends to be high which indicates the affinity of OTC to sorb to the soil; however, as the concentration increased, the sorption sites became saturated and prevented more OTC from being sorbed. Furthermore, n values which are presented in Table 3.3 indicated a freundlich constant n < 1 which confirms the observation of saturated sites and the more OTC added, the more difficult to find available sites for binding. This is due to the presence of weak sorption energy. In terms of the value of the freundlich sorption coefficient in the presence of Brij 35, K_f shows the highest value when the surfactant is present as monomers (below CMC at 0.02 g L^{-1}). As a result of increasing the concentration of Brij 35 to 0.25 g L^{-1} (about 2.5 CMC), the K_f value decreased and by increasing the surfactant concentration up to 5 g L^{-1}, the continuous decrease of K_f value is observed. This can be explained by the fact that at this high concentration, the surfactant is present in the solution in the micellar form which may facilitate the release of sorbed OTC into the solution.

The distribution coefficient (K_{oc}) values have been used as an indicator of the leaching potential of herbicides such as atrazine and metribuzin (Southwick et al., 1995). The calculated K_{oc} values show a higher leaching potential for OTC in the presence of Brij 35 (417.61 - 698.86) compared to the value of 844.10 in the absence of Brij 35.

Studies indicated that OTC has a great affinity to sorb to soil and clay (Sithole and Guy, 1987; Rabolle and Spliid, 2000); besides, it has a strong ability to chelate with monovalent and multivalent cations in soil organic matter and inorganic minerals by forming metal complexes which are considered the main reason for the immobility of OTC in soil (Martin, 1979; Figueroa and Mackay, 2005). However, under certain pH conditions, tetracyclines can be released from soil (Sithole and Guy, 1987; Mackay and Canterbury, 2005). The obtained K_f values are found to be within the range reported by Jones et al. (2005). In the present study, K_f values were found to be 23.55 in the absence of Brij 35. However, K_f values are reduced noticeably to reach 12.76 and 14.53 in the presence of Brij 35; this shows low sorption ability. It should be noted that K_f value in the presence of Brij 35 below CMC (in the monomer form) is slightly higher than K_f value in the water solution with no surfactant because the presence of monomers can increased the affinity of Brij 35 to sorb to soil and hence no solubilization effect was observed. Given the fact that surfactants are amphiphilic compounds, they sorb to soil after application. The sorption of nonionic surfactants onto soil has been studied (Kuhnt, 1993; Beigel et al 1998; Shen and Yen, 1999; Shen, 2000; Paria, 2008).

Soil analysis showed that the zero point of charge (zpc) was achieved at a pH of about 3.4 and since the pH of our soil solution is 5.7, it is expected that soil surface would be negatively charged. Consequently, the dominant species of OTC is the zwitteronic $OTC^{0\ -\ +}$ (at pH 3.3 -7.3). This leads to an increase in OTC sorption due to either electrostatic attraction or hydrogen bonding with soil surface (Sun et al. 2012).

Table 3.3-Distribution coefficient K_F, n, R^2 and K_{oc} values for OTC sorption in the presence of the nonionic surfactant, Brij 35

Concentration of Brij 35 (g L^{-1})	**K_F**	***n***	**R^2**	**K_{oc}**
0	23.55 ±1.03	0.49 ± 0.02	0.95	844.10 ±21.34
0.02	25.46 ± 1.54	0.45 ±0.03	0.93	912.84 ± 31.96
0.25	19.49 ± 0.51	0.48 ±0.01	0.97	698.86 ± 10.48
2.5	12.76 ±0.30	0.60 ±0.01	0.96	457.61 ± 6.28
5	14.53 ± 0.34	0.57±0.01	0.98	520.82 ± 6.88

This is consistent with our results that showed high sorption coefficient of OTC in aqueous medium compared to the soil-water surfactant system, and confirms the relatively low mobility of OTC in soil (Log P= -1.12), as indicated by Herbert and Dorsey (1995).

However, in the presence of the non-ionic surfactant (above CMC), OTC exhibited low affinity to sorb to soil. This can be explained by the fact that above zpc, more donor sites are available. Therefore, hydrogen bonding interactions are promoted between the surfactant micelles and the soil surface resulting in a competition between Brij 35 and OTC for sorption sites. Additionally, the formation of micelles can further enhance OTC release in the solution. Therefore, in the presence of the surfactant monomers, greater sorption was observed.

As a matter of fact, nonionic surfactants at concentrations above CMC decreased the sorption coefficient (k_d) values as the surfactants micelles in the aqueous phase compete with soil sorbed surfactants; they then become an effective partitioning medium for hydrophobic organic compounds (HOCs) leading to decreasing in k_d values (Sun et al., 1995). Similarly, the effect of Brij 35 on the adsorption of atrazin was found to be proportional to the concentration. Since Brij 35 competes with atrazin for sorption sites in the soil, increasing the concentration will enhance the admicelles on the clay surface and in turn, dissolve atrazin (Chappell et al., 2005). The mobility of OTC in the water-soil- surfactant system is presented in (Fig.3.3). Generally, the aqueous concentration of OTC increased slightly below CMC and subsequently, the concentrations exhibited a sharp increased once CMC was exceeded. To explain this behavior, it is known that monomers are present in the solution when the surfactant concentrations are below CMC so the surfactant favored to sorb onto soil in higher concentrations. This eventually led to more OTC sorbed to soil but once CMC was reached, micelles present in the solution then compete with sorbed surfactant for OTC. The more micelles in the aqueous phase, the more OTC partitioning into the micelles within the solution resulting in higher concentrations released from sorbed OTC. This result matches the findings of Sun et al. (1995) and Wang and Keller (2008).

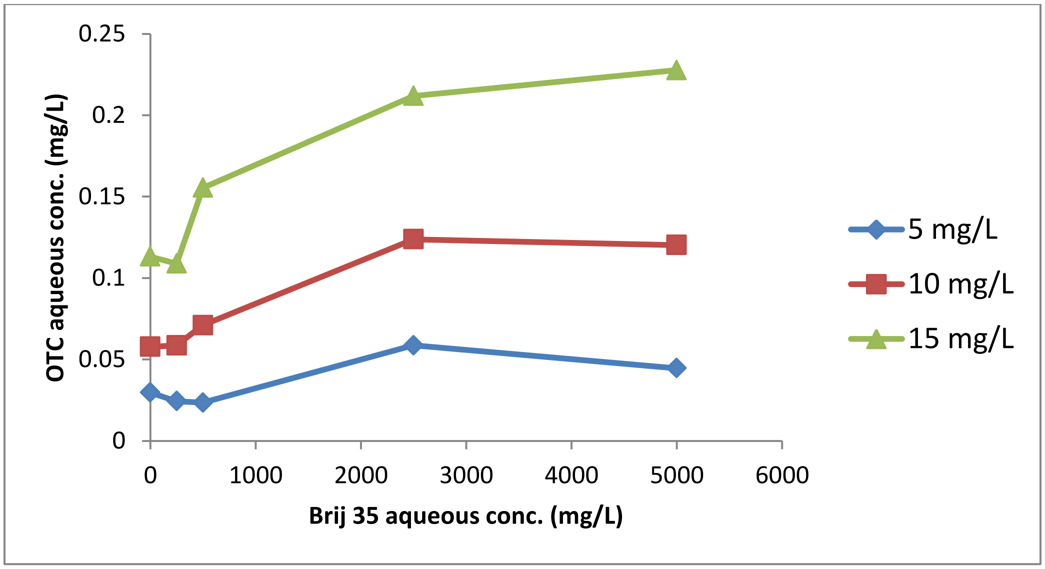


Figure 3.3 Dependence of the aqueous concentration of OTC on the total concentration of the non-ionic surfactant (i.e., monomers and micelles)

3.3.2. Mass balance

The mass balance for OTC is presented in Table 3.4. For all irrigation treatments, OTC concentrations were found to be below the detection limit by day 90. In both the water and surfactant-irrigated treatments, the total amount of OTC detectable in the system (soil + leachate), declined from an initial (applied) level of about 35 mg to less than 5 mg after 63 days and four irrigations. The relative amount of OTC in the two lower soil layers (15-45 and 45-70 cm) to that in the upper layers (0-5 and 5-15 cm) was at least 2-fold greater in the presence of surfactants from Day 21 onwards, suggesting that a greater amount of OTC leached downwards in the presence (*vs.* absence) of the surfactant. This will be addressed further in the discussion of OTC residue concentrations in the soil which follows.

From 21 days onward, the total quantity of detectable OTC was consistently greater in the surfactant treated columns than in those receiving tap water (Table 3.4). After 60 days, the total remaining OTC was 1.5 and 4 fold greater in the 5 and 0.5 g L^{-1} treatments, respectively, than in the tap water treatment. The percentage of unrecovered OTC (Fig.3.4) was similar for the irrigation types up to 21 days except for the treatment of Brij 35 0.5 mg L^{-1} which showed higher percentages (before dropping again after the second irrigation) compared to other treatments; however, later values were lesser in the presence of surfactant at 5 mg L^{-1}. In order to explain that, we should point out that the presence of the nonionic surfactant Brij 35 resulted in greater recovery compared to the tap water treatment. Despite the fact that OTC is immobile in soil under 5 cm (Blackwell et al., 2009), in the present study, 0.76% of the applied OTC was recovered in the leachate of the lysimeters irrigated with tap water, and 6.47 and 3.86%, respectively, for the 0.5 and 5.0 g L^{-1} surfactant solutions.The treatment differences in terms of the amount of unrecovered OTC (Fig 3.4) indicate the existence of factors, other than leaching, in the loss of OTC in soil. These factors could include sorption, microbial degradation (Yang et al., 2009) and photodecomposition (Zhang et al., 2012). The fact that less OTC was recovered in the presence of surfactant indicates the effect of the surfactant on the degradation of OTC in soil. Studies have shown that the presence of surfactant can increase the bioavailability of pesticides and hence, accelerate their degradation in the soil (Bardi et al., 2000).

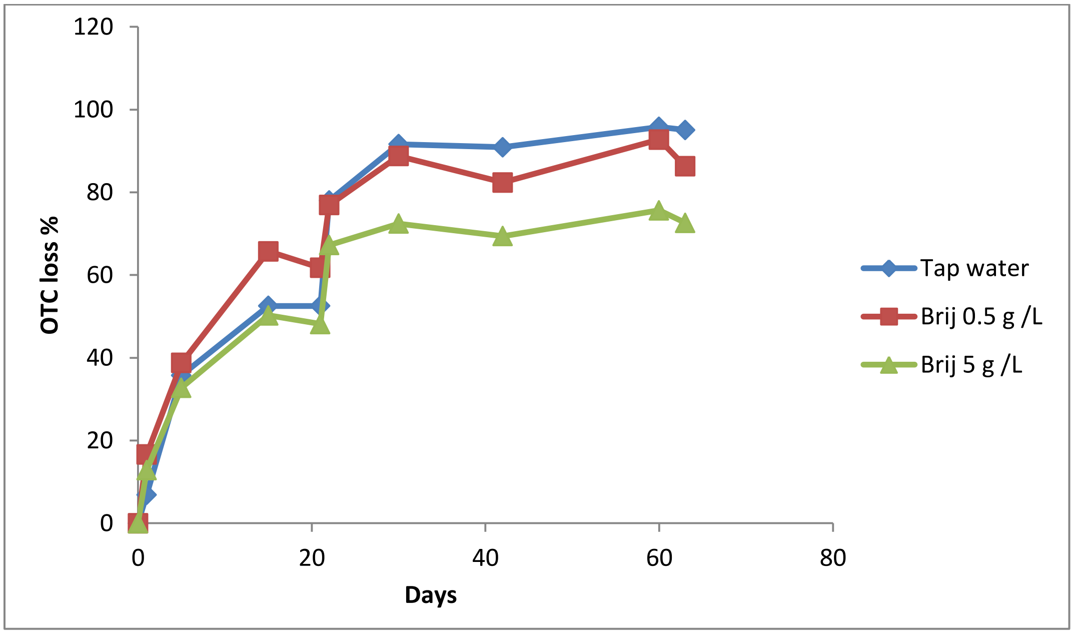


Figure 3.4 OTC lost percentage in the season in the absence and presence of surfactant

Similarly, Zhu et al. (2010) found that Brij 30 is capable of increasing the bioavailability of PAHs in the soil by enhancing the total abundance of bacteria. Recently, Zhang and Zhu (2012) reported that Tween 80 enhanced the sorption of pyrene on the bacterial cells and promoted degradation. However, in the present study, the presence of surfactant reduced, rather than enhanced, the loss of OTC (with lesser unrecovered amounts in the treatment of Brij 35 at concentration of 5 g L^{-1}). This is consistent with the findings of Yoshioka and Stella (2002); they studied the effect of surfactants on the degradation of Beta - Lactam antibiotics and reported that inhibition of acid degradation of propicillin was observed in the presence of non- ionic surfactant Brij 35 (above CMC). On the contrary, anionic surfactants promoted degradation.

Table 3.4 Amounts of oxytetracycline (mg) in different soil profile depth ranges, cumulated in leachate, and overall, over a 63 day period. (— implies that OTC was below detection levels)

Day	Irrigation solution																	
	Soil profile depth range (cm) / Cumulative leachate / Total ± *SD																	
	Tap water						Brij 35 @ 0.5 g L^{-1}						Brij 35 @ 5 g L^{-1}					
	0-5	5-15	15-45	45-70	Cum. leachate	Total	0-5	5-15	15-45	45-70	Cum. leachate	Total	0-5	5-15	15-45	45-70	Cum. leachate	Total
0	32.3	— Irrigation I —			0.00	32.25 ±0.63	35.5	— Irrigation I —			0.00	35.52 ±1.20	34.6	— Irrigation I —			0.00	34.56 ±0.92
1	29.8	0.24	—	—	0.00	30.04 ±0.38	25.1	4.23	—	—	0.29	29.61 ±0.88	21.5	7.02	—	—	0.41	28.98 ±0.59
5	20.7	—	—	—	0.00	20.71 ±0.50	13.4	8.04	—	—	0.29	21.75 ±0.88	9.47	10.4	—	—	0.41	20.29 ±0.45
15	9.25	6.05	—	—	0.00	15.30 ±0.20	4.64	1.44	5.77	—	0.29	12.16 ±0.58	4.71	4.6	2.95	—	0.41	12.67 ±0.56
21	—— Irrigation II ——				0.00	15.30 ±0.49	—— Irrigation II ——				1.42	13.58 ±0.69	—— Irrigation II ——				0.90	13.57 ±0.63
22	4.09	0.75	2.25	—	—	7.09 ±0.31	2.54	0.6	1.82	1.8	1.42	8.19 ±0.29	2.28	0.17	1.21	0.69	0.90	5.26 ±0.46
30	1.84	0.5	0.35	—	—	2.69 ±0.15	1.42	—	0.09	1.04	1.42	3.98 ±0.17	0.66	—	—	1.44	0.90	3.00 ±0.13
42	—— Irrigation III ——				0.24	2.93 ±0.19	—— Irrigation III —				2.27	6.25 ±0.39	—— Irrigation III ——				1.32	4.32 ±0.30
60	0.49	0.2	0.41	—	0.24	1.34 ±0.08	—	—	—	0.3	2.27	2.57 ± 0.13	—	—	—	0.28	1.32	1.60 ±0.13
63	—— Irrigation IV ——				0.24	1.10 ±0.04	—— Irrigation IV —				2.30	4.87 ±0.29	—— Irrigation IV ——				1.32	2.92 ±0.19

* SD stands for standard deviation

Furthermore, the more hydrophobic the surfactant, the greater its inhibition effect on the antibiotic's breakdown. Recently, Mohammed-Ali (2012) reported that the non-ionic surfactant Tween-80 increased the stability of tetracycline solution. He indicated that, as a result of the formation of micelles, tetracycline molecules were captured by the micelles which prevented them from degradation to anhydrotetracycline.

3.3.3. Effect of Brij 35 on the OTC residues in soil

The downward movement of OTC in sandy soil was assessed in the presence of Brij 35 in the irrigation water and compared with tap water irrigation. Figures 3.5, 3.6, 3.7 and 3.8 show the average concentrations of OTC in soil over the ninety day period for topsoil 0.1, 0.3 and 0.6 m soil depth. The concentration of OTC exhibits different trends by depth. As expected, the concentration at the soil surface was the highest in all treatments then decreased at greater depths. At the soil surface, the concentration decreased as the degradation rate increased with time; the concentration right after application was 3.38, 3.30 and 3.2123 µg g^{-1} in the tap water, Brij 35 0.5 and Brij 35 5 g L^{-1}, respectively. At day 15, the concentration decreased significantly in the tap water (0.96 µg g^{-1}) when compared to both treatments with surfactant (0.43 and 0.44 µg g^{-1}). The results showed that OTC degraded over time to reach 0.05 µg g^{-1} for tap water at day 60 whereas OTC was not detected in the treatments and by day 90, the OTC concentration was under the detection limit in samples taken from the tap water as well as for the surfactant treatment.

At 0.1m depth, OTC concentrations in the surfactant treatments had an upward trend during the first 11 days followed by a sharp decrease; however, concentrations in the tap water increased from day 22 and then, decreased gradually to be non-detectable by day 90. At 0.3 m depth, the trend was similar to the 0.1 m depth in all three treatments. This means that even with the tap water, OTC is still detected in soil samples and this is consistent with Hamscher et al. (2002). They carried out a field study to investigate the fate of tetracyclines in soil fertilized by liquid manure and found that the detected concentrations of TCs increased by depth from 171.7 μg kg^{-1} in the 20–30 cm layer comparing to 86.2 μg kg^{-1} in the top soil (0–10 cm). However, at the 0.6 m depth, considerable concentrations (20 μg kg^{-1}) of OTC were detected in the surfactant treatment only by day 22 then OTC concentrations decreased gradually in the surfactant treatment to (4.43 μg kg^{-1}) by day 60 while in tap water treatment, concentrations were under the detection limit. Moreover, the downward movement of OTC was significant in the treatment with Brij 35 0.5 g L^{-1} compared to the treatment of Brij35 5 g L^{-1}. The decrease in the concentrations of OTC by time and depth indicates that OTC moved downwards in soil while at the same time it degraded over the ninety day period. Such a decrease is reflected as the significant effect ($P \leq 0.01$) of treatment, depth, time and interaction among these factors (Table 3.5).

Given that OTC is strongly sorbed to soils, the enhanced mobility of OTC in soil in the presence of surfactant as compared to tap water may be due to the interaction between soil and surfactant. As indicated earlier, the sorption of nonionic surfactants onto soil is an important factor and may result in competition between Brij 35 and OTC for binding sites in the soil organic matter. This assumption is in agreement with the findings of Chefetz et al. (2008) who studied the effect of irrigation with secondary treated wastewater (STWW) on the environmental behavior of pharmaceutical compounds in soil columns and reported that naproxen was mobile in the soil irrigated with STWW. This behavior was the result of competition between DOM which present in the wastewater and naproxen for the binding sites. A similar conclusion was obtained by Kulshrestha et al. (2004) who stated that dissolved natural organic acids, such as humic acids, may compete with clay for oxytetracycline and thus, enhances its mobility in the soil profile.

In general, surfactants can increase the apparent water solubility of contaminants through their solubilization in the micelles, which form at concentrations above their CMC (Edwards et al., 1991). Depending on this concentration, contaminant properties, the degree and the location of solubilization in the micelle, surfactant effects can vary. Therefore, in our study, the concentration of Brij 35 above CMC has the potential to form micelles which in turn, have the ability to react with soil organic matter (SOM) by sorption as well as increasing OTC solubilization in the aqueous solution.

Table 3.5 Repeated measures analysis of variance for oxytetracycline residues in soil

Effect	**Probability**
Treatment	< 0.0001 **
Depth	< 0.0001**
Treatment × Depth	< 0.0001 **
Time	< 0.0001 **
Treatment × Time	0.2031 ^{NS}
Depth × Time	< 0.0001 **
Treatment × Depth × Time	< 0.0001 **

* denotes significant difference ($P \leq 0.01$),^{NS} denotes insignificant difference ($P \leq 0.01$)

The observed downward movement of OTC in the lysimeters from the surface to 0.6 m depth can be explained by the fact that Brij 35 is competing efficiently with OTC for sorption sites, while above the CMC, the lipophilic end (alkyl chain) of the surfactant molecule aggregate together inside the micelle, with the hydrophilic end point towards the aqueous phase on the exterior (Cheah et al. 1998). It is assumed that the polar moiety of Brij 35 (the exterior) could interact with the negatively charged sites in soil thus occupying the sites that otherwise would be available for interaction with the functional groups of OTC.

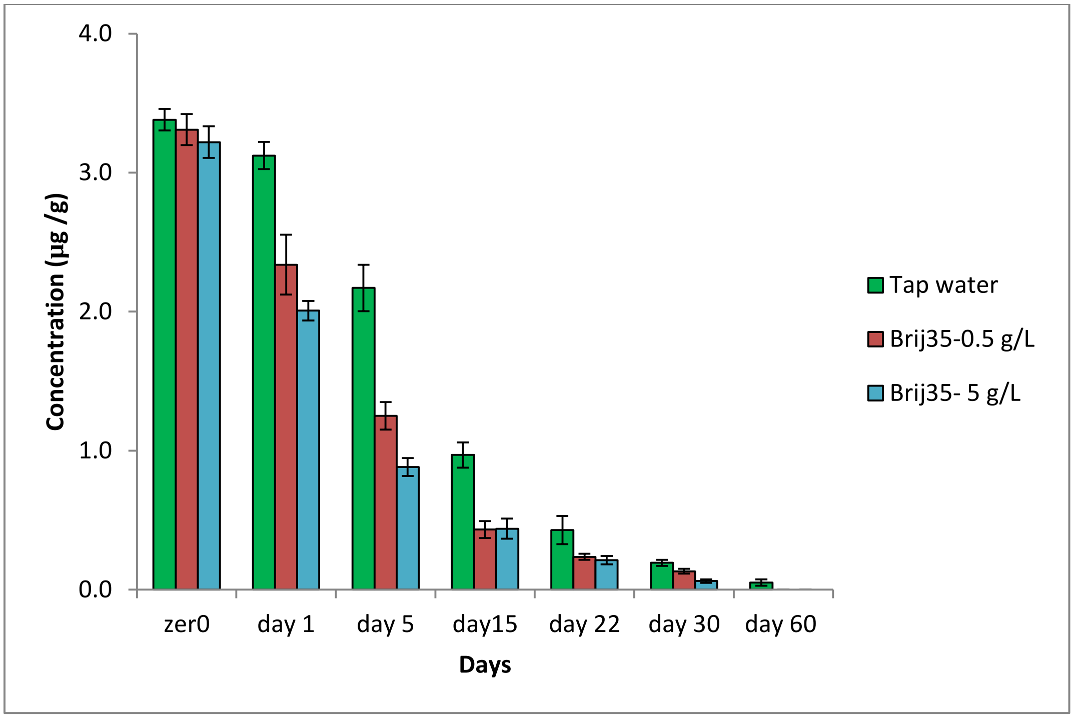


Figure 3.5 Oxytetracycline concentration in the soil at the surface

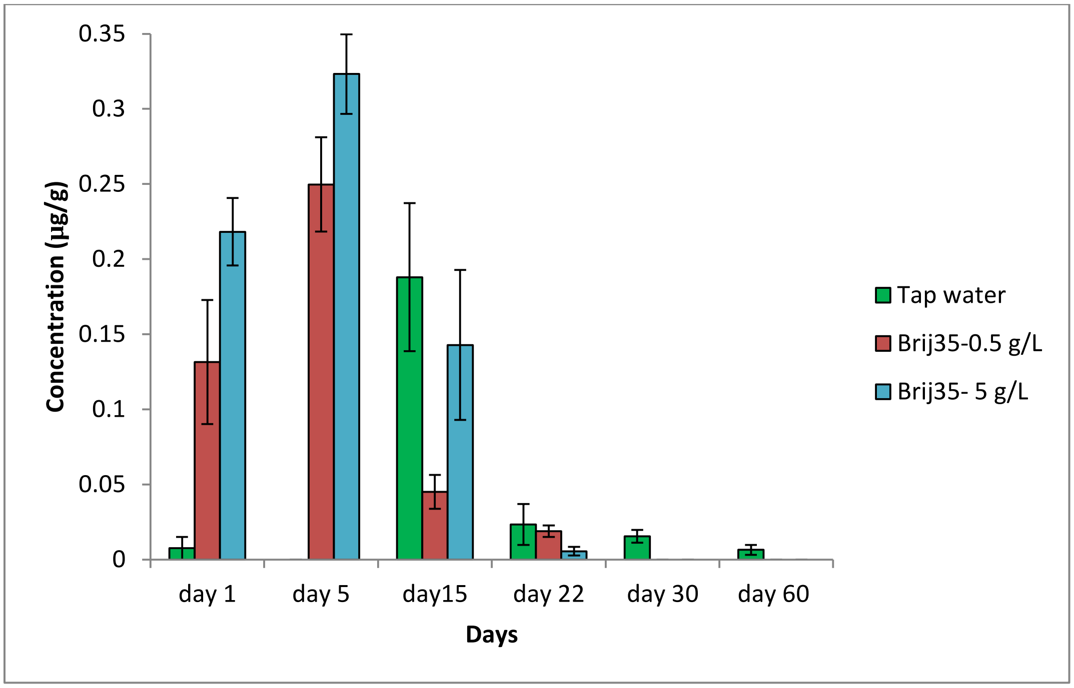


Figure 3.6 Oxytetracycline concentration in the soil at 0.1 m depth

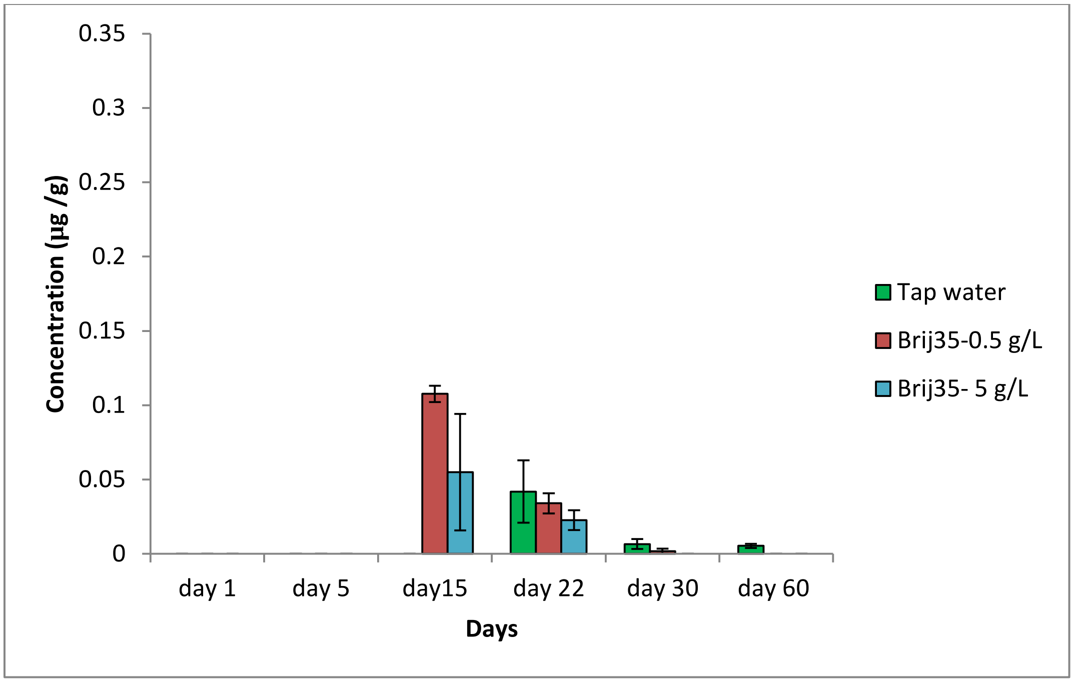


Figure 3.7 Oxytetracycline concentration in the soil at 0.3 m depth

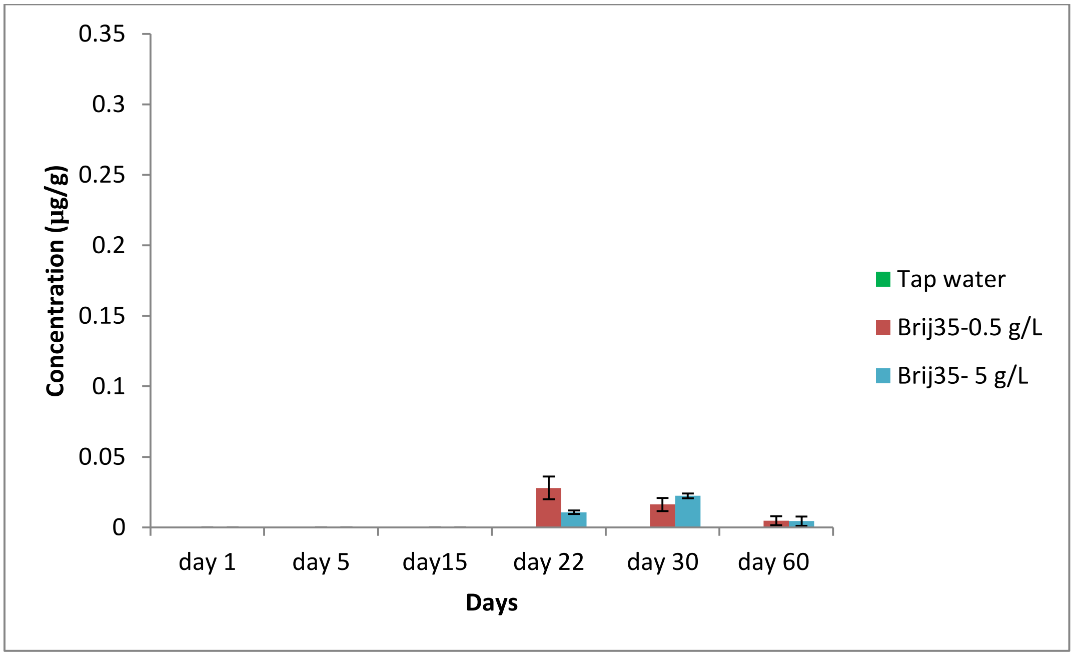


Figure 3.8 Oxytetracycline concentration in the soil at 0.6 m depth

Due to this behavior, OTC would exhibit weak sorption energy with soil. Another reason that may contribute to the Brij 35 competition for soil sites is the huge molecular size (1199.55) compared to OTC (284.72) (Yong and Mulligan, 2004). Furthermore, Muller et al. (2007) reported that wastewater irrigation was found to enhance the mobility of contaminants such as pesticides. They also stated that the presence of surfactants in the irrigation water is considered as a key factor in the promotion of the leaching potential of pesticides. Additionally, non-ionic alcohol ethoxylates (AE) are found to enhance the mobility of pesticides when applied at high (*vs.* low) concentrations to soil columns (Huggenberger et al., 1973). On the other hand, studies have shown that repeated applications of manure on soil as a fertilizer not only can lead to the release of bound tetracyclines from the soil and consequently increase its downward movement through soil (Kulshrestha et al., 2004) but also it poses a risk factor for public health as it may enhance the transfer of antibacterial-resistant bacteria to humans through water or plants (Sengelov et al., 2003).

3.3.4. Effect of surfactant on OTC residues in water

The leachate samples were analyzed to quantify the amount of oxytetracycline leached in the shallow ground water. OTC concentrations were higher in the leachate in both treatments with Brij 35 ranged from (102.72 - 2.72) and (49.66 - below detection limit) µg L^{-1} for Brij 35 0.5 and Brij 35 5 g L^{-1}, respectively. (Fig.5.9). In addition, statistical analysis indicated that a considerable concentration of OTC in the treatment with Brij 35 0.5 g L^{-1} was observed when compared to the treatment with Brij 35 5 g L^{-1}. On the other hand, the OTC concentration was non-detectable in the leachate of the tap water except for the third application (38 days after the beginning of the season) OTC concentration was 35.23 µg L^{-1}; this may have leached into the ground water through macrospores, generated by earthworms and the plant root system. In the present study, the maximum concentration in the leachate (102.72 µg L^{-1}) was higher than the concentration of 72 μg L^{-1} which was detected in the surface water near the plots which were treated with OTC-contaminated manure (Kay et al., 2005).

The presence of OTC in the leachate in the treatment with both concentrations of Brij 35 may have two possible explanations. First, Brij 35 has the ability to form micelles which dissolve OTC and increase its mobility after each irrigation event. Second, the effect of surfactant on soil properties; several studies have been conducted in this area of research (Koren, 1972; Abou Zreig, 1999; Singh and Kumar, 2000). They concluded that nonionic surfactants increased the water movement by increasing soil dispersion. Similar findings were reported by Tao et al. (2006) who confirmed that soil dispersion as a result of the presence of surfactants, increased the sorption sites and played an important role in contaminants movement. Furthermore, nonionic surfactants enhance the infiltration by increasing water penetration due to their ability to increase soil dispersion (Abou-Zreig, 2003; Katagi, 2008).

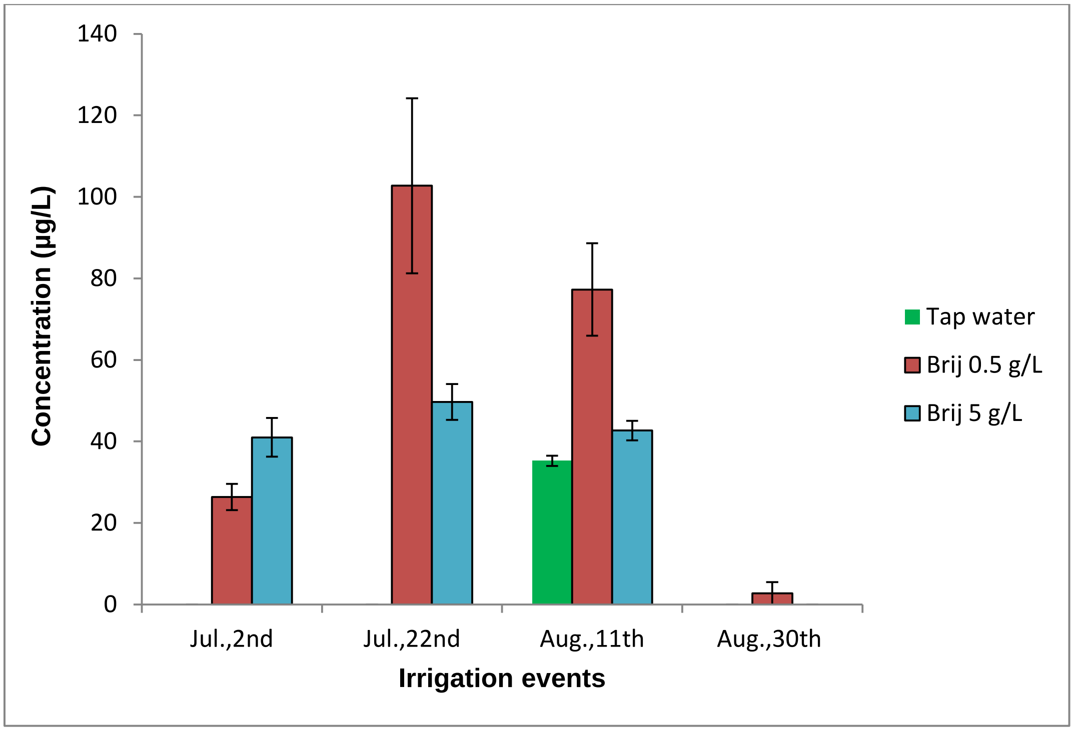


Figure 3.9 Oxytetracycline concentration in the leachate

Since nonionic surfactants are known for their ability to release pesticides from aged soils, Mata Sandoval et al. (2000) reported that Triton X-100 showed good desorption efficiency of pesticides from soil by replacing the pesticide on the sorption sites of soil particles and releasing it from soil. Xiarchos and Doulia (2006) stated that the ability of solubilizing polar compounds is positively linked to the hydrophilicity, and this hydrophilicity is known to be governed by the number of oxyethelyne groups (EO) in the molecule, i.e., the greater the number of EO groups, the more hydrophilic the surfactant (Jafvert et al., 1994). Since Brij 35 has twenty-three EO groups, it is expected to exhibit a high capacity to solubilize polar compounds. In terms of OTC structure, Hayes et al. (2007) indicated that OTC contains polar functional groups such as the cationic amide and ortho - substituded anionic groups which play an important role in the binding process of OTC and soil. When the cationic amide group attaches to the soil surface it increases the closeness of the ortho anionic moiety to the negatively charged surface which cause repulsion and hence decrease OTC sorption. They also found that the constant of binding is higher when OTC interacts with an aromatic acid versus an aliphatic acid. This supports the results obtained by our study. Because Brij 35 has a long aliphatic structure represented by the oxyethelyne group $(CH_2\ CH_2\ O)_{23}$ which may explain the leaching behavior of OTC in this study.

Conclusions

Understanding the mobility of Oxytetracycline within the soil-water-surfactant system is an important step in assessing the risk resulting from irrigation with wastewater. The present study showed that the presence of nonionic surfactant (Brij 35) in concentrations higher than its CMC increased the downward movement of OTC in the soil profile, presumably due to the solubilization power of micelles in the soil-water system when Brij 35 was present at 0.5 or 5 g L^{-1}. In addition, the presence of Brij 35 significantly increased the leaching potential. These findings were supported by the sorption test which indicated that K_f values for OTC were significantly lower in the presence of the nonionic surfactant.

Despite the fact that lysimeter studies have shown OTC to seldom move beyond 10 cm depth in the soil profile, our study indicates that the presence of a nonionic surfactant in irrigation water promoted the mobility of OTC in soil and led to its presence in leachate at a depth of 1 m below the soil surface. Therefore, the continuous use of wastewater containing nonionic surfactants at concentrations exceeding their CMC can be expected to increase the likelihood of OTC being found in leachate, eventually reaching ground water, and potentially contaminating water resources. This study highlights the role played by the application of OTC-contaminated manure as is a common practice; it does not only increase the risk of OTC leaching but also results in the long term exposure of bacteria to antibiotics. This increases the risk of the bacteria becoming resistant to antibiotics as well as increasing the likelihood of transferring the bacteria resistance to humans. This could become a momentous issue, as many antibiotics, including OTC, remain biologically active in the soil for weeks or months.

Connecting Text to Chapter 4

Ionophores are used only for veterinary purposes mainly as growth promoters; therefore, they are known as markers for contamination originating from agricultural sources. They can be introduced to soil by applying contaminated manure. Since surfactants could be present in the irrigation water, the need for assessing the risk from the presence of surfactants and ionophores in soil is of much importance. Therefore, in this chapter, we investigated the fate of an ionophore, monensin in the presence of a non-ionic surfactant, Brij 35, in irrigation water. In line with the previous chapter, a sorption experiment was also conducted in the laboratory.

This chapter is a manuscript submitted for publication to the journal of Agricultural Water Management. The manuscript is co-authored by my supervisor, Dr. S. O. Prasher. The format of the original draft has been modified to remain consistent with the thesis format. All literature cited in this chapter is listed in the Bibliography (Chapter 9), at the end of the thesis.

Chapter 4 – Fate of Monensin in the Presence of Nonionic Surfactant Brij 35 in Sandy Soil

Eman ElSayed and Shiv Prasher

Abstract

As fresh water is a limited resource in many parts of the world, the use of wastewater for irrigation has become an important alternative. Therefore, many countries facing a water deficit, use partially treated, or even untreated, wastewater. This may increase the input of many contaminants into the environment. In the present study, we investigate the effect of using surfactant rich water in irrigation on the mobility of the most commonly-used veterinary antibiotic, monensin. Nine PVC lysimeters, 1.0 m long x 0.45 m diameter, were packed with a sandy soil to a bulk density of 1.35 Mg m^{-3}. Cattle manure, containing monensin, was applied at the surface of the lysimeters at the recommended rate of 10 t/ha. Each of three aqueous Brij 35 solutions, 0, 0.5 and 5 g $L^{-1,}$ were applied to the lysimeters in triplicate. Over a 90 day period, soil and leachate samples were collected and analyzed. The results of the laboratory sorption experiment showed that when the nonionic surfactant Brij 35 is present, the sorption coefficient of monensin was reduced significantly from 120.22 mL g^{-1} in the aqueous medium to 112.20, 100 and 63.09 with Brij 35 concentrations of 0.02, 0.25, 2.5 and 5 g L^{-1}, respectively. The lysimeter results indicated a significant downward movement of monensin at depths of 60 cm in the soil profile and leachate in the presence of the surfactant. Thus, the continuous use of poor quality water could influence the transport of monensin in agricultural soils, and consequently, pose a risk for groundwater pollution.

Introduction

Wastewater treatment plants (WWTP) are considered one of the main non-point sources for spreading emerging contaminants (ECs) in the environment. Among ECs, antibiotics are one of the most abundant contaminants detected in WWTP effluent (Jones et al., 2001; Heberer, 2002; Miao et al., 2004; Batt et al., 2007; Gulkowska et al., 2008; Kummerer, 2009; Fatta-Kassinos et al., 2011). Due to the extensive use of antibiotics for both human and veterinary purposes, these compounds are released constantly in the environment and could increase the risk of developing antibiotic resistance genes (Schwartz et al., 2006; Kummerer, 2009). Consequently, they contribute to the reduction of the therapeutic potential of some drugs currently administered to human and animals (Kemper, 2008). The elimination of antibiotics in WWTP depends on the chemical properties of the antibiotic and the type of treatment used in the WWTPs. Sorption to activated sludge is considered an effective elimination method for hydrophobic antibiotics. However, antibiotics are designed to be hydrophilic; they remain in the liquid phase in WWTP effluent and eventually, they may be discharged into surface water.

Ionophore antibiotics are used extensively in veterinary agriculture to prevent coccidiosis in poultry and as a growth promoter for cattle. Monensin (MON) is an ionophore antibiotic; it is a monocarboxylic polyether primarily produced by Streptomyces. When the monensin molecule is ionized, the carboxylic group becomes charged in order for it to be neutralized; hydrogen bonding between the molecule and monovalent cations are formed resulting in a complex. This zwetterionic structure provides the molecule with an extra hydrophobic exterior (Gertenbach and Popo, 1975). This chelation potential allows monensin to disrupt the ion gradient of the cell membrane of microorganisms causing cell scrambling and shrinking and ultimately leading to death (Shen and Brodbelt, 2000; Lopes et al. 2002; Kiehl et al., 1998). Although monensin is toxic to humans and causes acute renal failure leading to a patient’s death (Caldeira et al., 2001), recently, monensin was reported to be one of the potential drugs to be used at the nano molar level to prevent prostate cancer cell growth (Ketola et al., 2012).

In the environment, monensin is vulnerable to breakdown by hydroxylation, O-demethylation, and/or decarboxylation reactions to more than 50 metabolites, which are similar to the structure of the parent compound (Donoho, 1984; Donoho et al., 1982). MON concentration was found to be 2000 µg kg^{-1} in the fraction of suspended solids. Mon concentrations are detected in surface water as high as 1.2 µg L^{-1} and up to 30 µg L^{-1} in sediments near agricultural regions. MON is reported to be immobile in the soil (Carlson and Murray 2006; Donoho, 1984). The reported distribution coefficient (K_d) ranges from 0.915 to 78.6 (L kg^{-1}) for different types of soils (Sassman and Lee, 2007). The reported half-life ranges from 3.3-3.8 days under field conditions to 13.5 days in the laboratory (Sassman and Lee, 2007; Carlson and Mabury, 2006). Being hydrophobic, monensin is expected to strongly sorb to sediments, reducing the likelihood of moving down the soil profile.

Surfactants are another group of ECs frequently detected in wastewater (Brunner et al., 1988; Field et al., 1992; Wild et al., 1990). These compounds are amphiphilic molecules containing a polar group represented by an ethylene oxide head and a non-polar tail in a long alkyle chain. They have unique features; once they reach the point of critical micelles concentration (CMC), they tend to aggregate and form spherical shapes, called micelles. Among surfactants, non-ionic surfactants such as alcohol ethoxylates (AEOs) and alkylphenol ethoxylate (APEO) are widely used in cleaning products, detergents, and the textile industry; therefore, they are more likely to be detected in urban sewers (Conn et al., 2006; Loyo-Rosales et al., 2007; Stuart et al., 2012). During wastewater treatment, the hydrophilic heads are shortened and transformed into monoethoxylate (NP1EO) and diethoxylate (NP2EO). These compounds are totally deethoxylated to NPs which are more hydrophobic and toxic as well as being more persistent. More importantly, these compounds are estrogenic to aquatic organisms at relatively low concentrations. WWTPs are not efficient in eliminating all of these metabolites (Loyo-Rosales et al., 2007). Consequently, nonylphenols (NPs) were detected at high concentrations ranging from 1.8 to 25 g L^{-1} in two rivers in Switzerland (Ahel et al., 1996). Also, NPs were detected at a concentration up to 2 g kg^{-1} in sludge from a WWTP receiving industrial wastewater (Minamiyama et al., 2006). In Kansas, concentrations up to 898 mg kg^{-1} of NPs have been measured in biosolides from WWTP (Keller et al., 2003). In the US, concentrations from 9.4-309 g L^{-1} of NPs were detected in the leachate (La Guardia et al., 2001). Interestingly, the presence of NPs in water can induce water-air volatilization; therefore, high concentrations were measured in the atmosphere in New York City up to 56.3 ng m^{-3} in coastal areas and 81 ng m^{-3} at suburban sites. This suggests that the presence of NPs in the atmosphere can negatively affect human health and pose a risk to the ecosystem in areas receiving treated sewage effluents (Van RY et al., 2000). It is apparent that there is a need to find another alternative to APEOs. The best substitute is found to be alcohol ethoxylates AEOs, which are less toxic than APEOs in terms of their estrogenic effect. They are biodegradable and yet in the environment, the intermediate product is less degradable than the parent compounds. Nevertheless, AEOs cannot replace APEOs in some industries; to achieve a similar efficacy, high levels of AEOs should be used (Campelle, 2002). Consequently, they will be more abundant in the WWTPs and could be released into the environment, depending on the performance of the treatment in WWTPs. The reported half-life for AEOs in soil was 30-40 days depending on the soil type and depth. Furthermore, for a given AE surfactant, the higher the number of ethelyne oxides (EO) units and this results in less degradation of the surfactant (Krogh et al., 2003).

Given the amphiphilic nature of surfactants, they can solubilize hydrophobic compounds in the environment (Huggenberger et al., 1973; Kan and Tomson, 1990; Aronstein et al., 1991; Rodriguez-Cruz et al., 2004). Generally, unlike cationic and anionic surfactants, non-ionic surfactants increased the downward movement of pesticides in soil. This was due to the lower CMC values, the higher level of surface-tension reduction and their significant solubilization capacity in dilute solutions (Paria, 2008). More specifically, Sanchez-Camazano et al. (1995) reported that non- ionic surfactants, at high concentrations, effectively increased the mobility of the herbicide, metolachlor, in soil; however, at low concentrations, metolachlor mobility was reduced. Similarly, Katagi (2008) indicated a greater mobility of pesticides in leached water at high concentrations of non-ionic surfactants. Further, Tao et al. (2006) indicated that non-ionic surfactants at low concentrations (0-20 mg L^{-1}) mobilize atrazine in the environment. Another input pathway for surfactants is the application of surfactant rich water (grey water) for irrigation, which changes the property of soil causing water repellence (Wiel-Shafran et al., 2006).

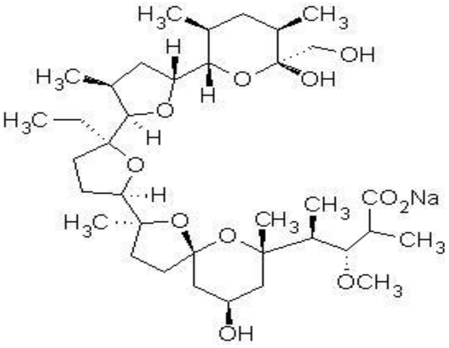
Agriculture accounts for over 70% of the world's water withdrawal (Raskin et al., 1997). About 40% of global crop production comes from 18% of irrigated agricultural lands and employs about 30% of the global population in rural areas. Water resources are limited in many parts of the world causing major water deficits. To bridge the gap between food demand and a growing population, wastewater has become an alternative option for irrigation in eighty-eight developing countries (IWMI, 2003). Water directly used from effluents could be partially treated or untreated (Chatterjee, 2008). Consequently, irrigation with this poor quality water may pose a risk for the contamination of water bodies. With the application of manure for fertilization, ionophores can be introduced to soil, which is irrigated with surfactant rich water. Eventually, this leads to the presence of two groups of contaminants in the soil: ionophores and surfactants. Information is lacking on the impact of non-ionic surfactants on the mobility of coexisting compounds such as ionophores. For this reason, laboratory and field experiments were conducted to investigate the effect of the non-ionic surfactant (Brij 35) on the downward movement of monensin in soil and water.

4.2 Materials and methods

4.2.1. Study compounds

Monensin A, HPLC grade from Sigma-Aldrich, solubility 4.8- 8.9 mg L^{-1} (Table 4.1) and a pure standard (Pestanal®) and formulation (Sencor 75) of metribuzin were purchased from Sigma-Aldrich. The non-ionic surfactant Brij 35 [Polyoxyethylene lauryl ether $(C_2H_4O)_{23}$-$C_{12}H_{25}OH$] with critical micellar concentration (CMC) = 74 mg L^{-1} and Log P is approximately 3.13 (HERA, 2009). HPLC-grade methanol and acetonitrile were obtained from Sigma-Aldrich. Mobile phase chemicals were purchased from Fisher Scientific. Double–deionized water (Milli-Q, Millipore, Molsheim, France) was used in the preparation of standard solutions and mobile phase solutions.

Table 4.1 Physical and chemical characteristics of Monensin

Physical - chemical properties	Chemical structure
Solubility : 4.8-8.9 mg L^{-1} MW : 671 g mol^{-1} Log K_{ow} : 2.8-4.2 [a] Pka : 4.2; 6.5[a]	

[a] Sassman and Lee (2006)

4.2.2. Soil characteristics

The sandy soil used in this experiment belongs to the St. Amable complex; it was obtained from a field in the Macdonald Campus of McGill University, Ste-Anne-De-Bellevue, QC. The physical and chemical properties of the soil are given in Table 4.2.

Table 4.2 Physical and Chemical Characteristics of Soil

Soil Type	Sand (%)	Silt (%)	pH	Bulk Density (Mg m^{-3})	Organic Matter (%)	CEC (cmol kg^{-1})	Hydraulic Conductivity (cm d^{-1})	Zero point of charge (zpc)
Sandy	92.2	4.3	5.5	1.350	2.97	4.9	1.67 (*S.D. = 0.45)	3.4

* S.D. stands for standard deviation

4.2.2.1. Batch adsorption experiment

Adsorption of MON onto soil particles in the presence of the nonionic surfactant Brij 35 was investigated through a soil equilibrium technique. Triplicate soil samples (1 g) were equilibrated with an aqueous solution (20 mL) of MON at concentrations ranging from 5 to 50 µg mL^{-1} in factorial combination with Brij 35 concentrations of 0, 0.02, 0.25, and 2.5 g L^{-1}. All solutions contained 0.01 M $CaCl_2$ to mimic the ionic strength of groundwater (Wilde et al., 2008). The soil slurry was placed in a 50 mL centrifuge tube, and placed on a shaker, for 48 hrs. The slurry was centrifuged at 2683 g for 20 min. Extraction and analysis of MON proceeded, as described above. The proportion of MON adsorbed was calculated by taking the difference between the amount initially present in the solution and the amount remaining in the solution after equilibrium with the soil.

4.2.2.2. Analytical procedure

A commercially available monensin ELISA kit was purchased from Beijing Wagner Biotechnology Co. Ltd. The ELISA kit was designed for analysis of monensin in animal feed and edible tissues. The kit consisted of a 96-well microtiter plate coated with a coupling antigen for monensin. The analysis was performed according to the manufacturer’s instructions. After the addition of standards and samples (25 µL), the monensin residual in the samples compete with the antigen in the microtiter plate for the antibodies. After a 40-min incubation period at room temperature, solutions were discarded, and non-bound components were removed by a series of three washings (250 µL) with phosphate-buffered saline (PBS) Tween. Next, a tetramethyle-benzidine (TMB) substrate (100 µL) was added to the plate and incubated at room temperature for 20 min to reveal the color. The reaction was stopped with the addition of 3N NaOH (50 µL). At that point, the color intensity was measured at 405 nm using a spectrophotometer. Standard/ solutions (0, 1, 3, 9, 27, and 81 µg L^{-1}) were provided with the monensin ELISA kit along with a high concentration standard control (1 mg L^{-1}). A seven-point standard curve was established for quantifying the monensin in the samples. Intra assay variability was determined by testing the samples in duplicate within a plate. Absorbance of the sample is negatively related to the monensin residual in each sample. Then, after comparing with the standard curve, the results were multiplied by the dilution factor in order to calculate monensin concentration in the sample.

MON sorption data were fitted to the freundlich adsorption isotherm equation:

$$q = K_F \, C_{aq}^{n} \qquad \text{Eq. 4.1}$$

Where

q is the amount of MON sorbed (μg g^{-1}),

C_{aq} is MON concentration after equilibrium in μg mL^{-1}, and

K_F , n are the Freundlich affinity and nonlinearity coefficients, respectively (mL g^{-1})

4.2.3. Field experimental set up

The field experiment investigating monensin transport in sandy agricultural soil was conducted in nine outdoor PVC lysimeters set up at the Macdonald Campus of McGill University, Ste-Anne-De-Bellevue, Quebec. The lysimeters (0.45 m O.D. × 1 m long) were sealed at the bottom with 0.6 m × 0.6 m PVC sheets. Each lysimeter was packed in layers with sandy soil and adjusted to a bulk density of 1.35 Mg m^{-3}. A 0.05 m diameter drainage pipe was installed at the bottom of each lysimeter. Four, 10 mm diameter soil sampling holes were made in each lysimeter at depths of 0.1, 0.3 and 0.6 m from the soil surface (Fig. 4.1). The lysimeters were protected to prevent the entry of natural precipitation.

4.2.3.1. Application of tested compounds

Antibiotic free manure was collected from a cattle farm in Ham-Sud, Quebec. At the end of June 2009, before the start of the experiment, all of the lysimeters were irrigated, bringing them to saturation. The drainage pipe at the bottom of each lysimeter was left open throughout the study.

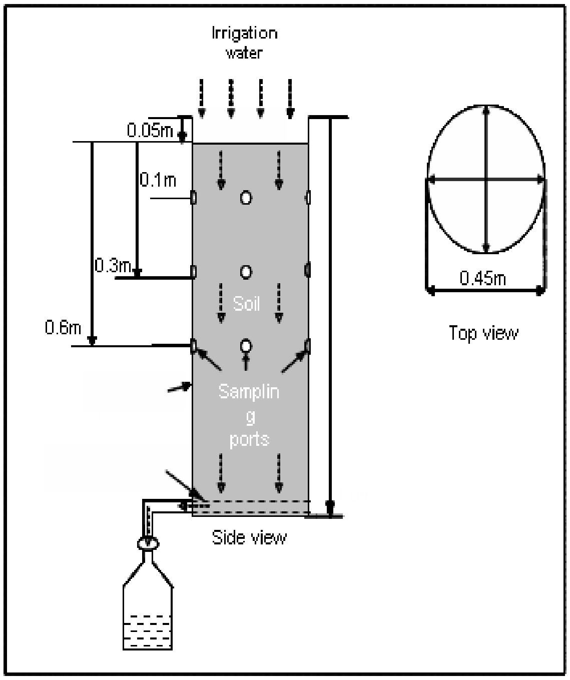


Figure 4.1 Schematic design of the lysimeter

The next day (Day 0), with the lysimeter's soil at field capacity**,** homogenized manure (10 Mg ha^{-1}) was applied to the surface of all of the lysimeters after being spiked with monensin and manually mixed into the top 30 mm of soil (Chettri and Thapa, 2004). The spiked concentrations were calculated after adjusting the amount of monensin extracted from the cattle manure (4.405 µg g^{-1}) to the area of the lysimeter and the amount of manure applied. This was done according to the findings of Dolliver et al. (2008). Metribuzin was then sprayed on the soil surface of each lysimeter (July 1, 2009) at the locally recommended rate for potatoes (1 kg a.i. ha^{-1}) as is common practice. Irrigation water (70 mm), containing one of three different concentrations of Brij 35 (0, 0.5 or 5.0 g L^{-1}) was applied at day 0, day 21, day 42, and day 63, according to the recommended irrigation practice for potatoes. Each treatment was replicated three times. While these surfactant concentrations may appear to be high, Abu-Zreig et al., (1999) have studied the effect of surfactants on atrazine movement in soil using concentrations up to 10 g L^{-1}.

4.2.3.2. Soil and leachate sampling

Soil samples were collected at the surface as well as at depths of 0.1, 0.3 and 0.6 m, through 4 sampling ports in the side of the lysimeters. The soil samples were collected on 8 occasions: 0, 1, 5, 11, 22, 43, 60 and 90 days after the application of manure. For each surfactant concentration, three replicate soil samples (3 lysimeters) were taken at each of the four depths, and samples from a common treatment × depth were combined in a composite sample (~15 g). Subsamples of about 5 g were taken from each composite sample, and their moisture content determined. The remaining portions of the samples were stored in sealed bags in a freezer at -24ºC until extraction. Leachate samples (1 L) were collected as a subsample of a total of approximately 11 L of leachate collected at the outlet at the bottom of each lysimeter following each of the four irrigation events. The subsamples were then transported to the lab and immediately extracted to prevent any chance of MON degradation.

4.2.3.3. Mass balance calculations

At each sampling date, the total antibiotics mass recovered from each lysimeter was calculated as the sum of the antibiotic recovered in the soil samples across all depths of the soil profile. Adding the antibiotic mass in the leachate to that in the soil would total the initial antibiotic mass applied, minus any losses (unrecovered MON) due to degradation or volatilization (Eq. 4.2).

$$MON_{init} = 1590.4\,\rho\,\left[C_{(0-5)}\Theta_{(0-5)}\,h_{(0-5)} + C_{(5-15)}\Theta_{(5-15)}h_{(5-15)} + C_{(15-45)}\Theta_{(15-45)}h_{(15-45)} + C_{(45-70)}\Theta_{(45-70)}h_{(45-70)}\right] + \left[C_{leach}V_{leach}\right] + MON_{lost} \tag*{Eq. 4.2}$$

where,

MON_{init}	Total monensin (mg) initially applied
MON_{lost}	Monensin lost through degradation, volatilization, etc. (mg)
ρ	Soil bulk density, (g cm^{-3})
$C_{(x-y)}\Theta_{(x-y)}h_{(x-y)}$	Monensin concentration and soil moisture content, respectively, in soil layer *h* ranging from depth *x* to depth *y* (mg g^{-1}).

C_{leach}	monensin concentration in leachate (mg L^{-1})
V_{leach}	Volume of leachate
1590.4	Soil layer surface area, $\pi \left(\frac{D}{2}\right)^2$, where D = 45 cm

In order to calculate the mass of monensin recovered in the soil layer samples, the following equation was used for this purpose:

$\text{Mass of MON} = [C\ (m)] * \rho * a * h$ Eq. 4.3

Where

C = laboratory reported analytical MON concentration in soil samples (mg g^{-1}),

m = moisture content of soil samples (mass water /mass dry soil mg g^{-1}),

ρ = soil bulk density (g cm^{-3}),

a = area of lysimeter (m^2) and

h = sampling depth of soil layers (cm).

The half-life $t_{½}$ of monensin was calculated as follows

$$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$ Eq. 4.4

Then equation 6 is used in order to calculate k

$$C = C_0\ e^{-kt}$$ Eq. 4.5

Where

C, monensin concentration at time (t);

C_0, the initial concentration of monensin and k is the degradation rate constant.

4.2.4. Extraction from leachate and soil samples

4.2.4.1. Leachate samples extraction

Leachate was extracted immediately following transport from the lysimeters. Each 1 L subsample was filtered through a 90 mm filter paper, followed by filtration through a 45 mm filter (Advantec, Japan) to remove coarse and fine suspended matter, prior to extraction. HLB cartridges from the Oasis Co. Ltd, NY were used in the solid phase extraction (SPF). Prior to extraction, 2g of EDTA were added to the sample. Preconditioning of each cartridge began by passing 5 mL of methanol through each cartridge twice, then 5 mL of 50:50 water: methanol (v/v), followed by 100% water, all at a flow rate of 10 mL min^{-1}. The sample filtrate was then passed through the cartridges and washed twice with 5 mL of methanol to elute MON. Collected in a test tube, the 10 mL of eluate was evaporated under a gentle stream of N_2, residue redissolved in 1 mL of acetonitrile, then passed through a 0.22 µm syringe driven filter (Millex - GV, Japan), and the filtered solution transferred to a vial for HPLC analysis.

4.2.4.2. Soil samples extraction

Ten grams of the soil sample were weighed in a 50 mL centrifuge tube and 20 mL of acetonitrile was added. The tube was vortexed for 30 seconds and placed in an ultrasonic bath for 20 min. It was then centrifuged at 2683 g for 20 min. Supernatant was decanted and the extraction procedure was repeated twice. The combined supernatants were passed through a 45 mm filter paper, and then evaporated under a N_2 stream. Samples were re-dissolved in 1 mL of acetonitrile and passed through a 0.22 µm syringe-driven filter prior to the bioassay analysis.

4.2.5. Data analysis

A statistical model using repeated measures over time and depth was employed to determine if the monensin concentrations differed between treatments, over time and with varying depths. The data was analyzed with PROC MIXED in SAS v. 9.2 (SAS Institute, Cary, NC).

4.3. Results and discussion

4.3.1. Effect of Brij 35 on the sorption of monensin

Adsorption plays an important role in the transport of chemicals in soil. To the best of the author’s knowledge, no study has been conducted to investigate the sorption behavior of monensin in the presence of the nonionic surfactant Brij 35. Therefore, a sorption experiment in the presence and absence of Brij 35 was carried out; the results demonstrate that the amount of MON sorbed was higher in the absence of Brij 35; however, it decreased in the presence of surfactant at concentrations above CMC.

Fig. 4.2 shows the sorption isotherms of MON in Bij35 solutions at concentrations (0, 0.02, 0.25, and 2.5 g L^{-1}). All isotherms obtained for MON fit well the Freundlich model Eq. (1), with R^2 values between 0.95 and 0.97. At low concentrations, sorption tends to be high which indicates the affinity of MON to sorb to the soil; however, as the concentration increased, the sorption sites became saturated and prevented more MON from being sorbed. Furthermore, the n values, which are presented in Table 4.3, indicated a Freundlich constant $n < 1$ which confirms the presence of saturated sites and weak sorption energy. The more MON added, the more difficult to find available sites for binding. The values of the Freundlich sorption coefficient in the presence of Brij 35, K_f show the highest values in the absence of the surfactant. The K_F values decreased as a result of increasing the concentration of Brij 35 gradually from 0.02 to 0.25 g L^{-1} (about 0.27 and 2.5 CMC, respectively). By increasing the surfactant concentration up to 2.5 g L^{-1}, a continuous decrease of K_F values is observed. This can be explained by the fact that at a concentration this high, the surfactant is present in the solution in the micelle form, which may assist in releasing the sorbed MON into the solution.

The ability to form complexes with monovalent cations is promoted in the presence of the hydrophobic form of MON. The degree of hydrophobicity depends on the process by which carboxylic acid’s negative charge becomes neutralized (Shen and Brodbelt, 2000; Kiehl et al., 1998). Therefore, MON exhibits a great affinity to sorb to soil and organic matter, suggesting that MON is immobile in soil. Sassman and Lee (2007) investigated sorption of MON. They calculated the Freundlich distribution coefficient in different types of soil, varying in organic matter content, and they found that values widely range from 0.94-42.7 L kg^{-1}. Recently, Ilhan et al. (2012) reported that MON is strongly sorbed to woodchip and the calculated K_F value was 161 L kg^{-1}.

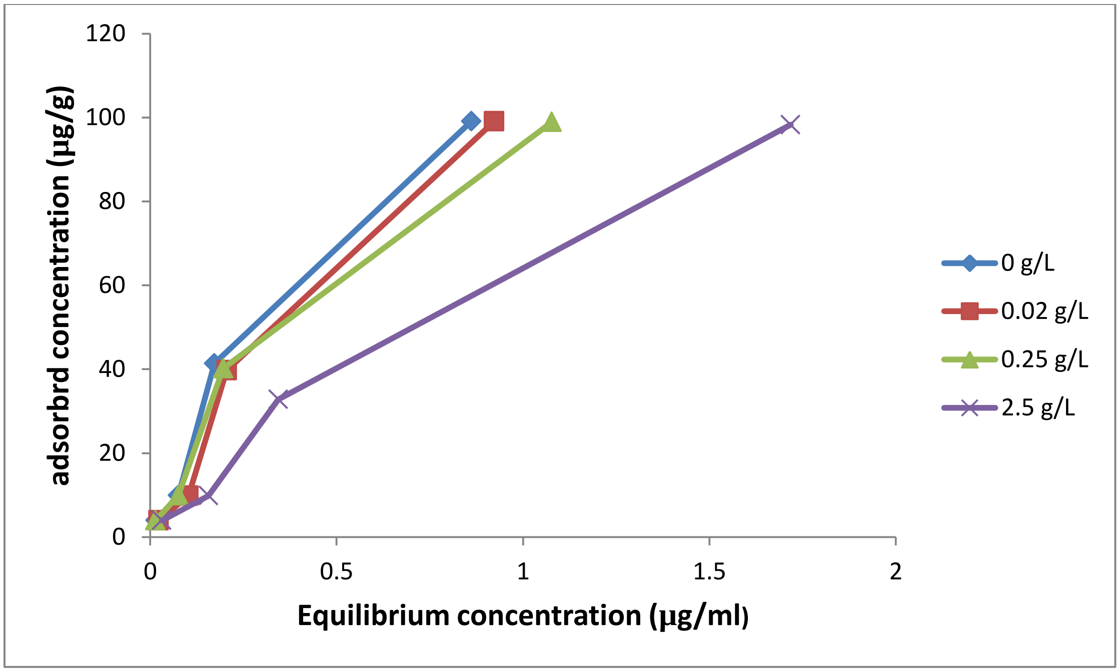


Figure 4.2 Monensin isotherms in the absence and presence of the non-ionic surfactant Brij 35

In the present study, K_F values were found to be 120.22 mL g^{-1} in the absence of Brij35. However, K_F values were reduced significantly ($P < 0.01$) to100 and 63.09 mL g^{-1} in the presence of Brij 35 at concentrations above CMC; this clearly showed the low sorption potential of MON in the presence of micelles. The K_F values found in the presence of Brij 35 below CMC (in the monomer form) are slightly lower than the K_F values in the aqueous solution with no surfactant. This observation may be attributed to the high affinity of monomers to sorb to soil and hence, occupy the available sites, resulting in the observed increase in the amount of MON in the solution.

The sorption of nonionic surfactants onto soil has been extensively investigated (Kuhnt, 1993; Beigel et al 1998; Shen and Yen, 1999; Shen, 2000; Paria, 2008). Since Brij 35 is a nonionic surfactant and MON is zwiteronic in the solution, it is assumed that MON is captured by the micelles in the solution and the remaining amount of MON was in competition with Brij 35 for binding sites.

Table 4.3 Distribution coefficient K_f, n, R^2 values for MON sorption in the presence of the nonionic surfactant, Brij 35

Brij 35 Concentration (g L^{-1})	K_F	n	R^2
0 (tap water)	120.22	0.83	0.95
0.02	112.20	0.9	0.95
0.25	100	0.77	0.96
2.5	63.09	0.82	0.97

The results of this sorption experiment are in agreement with Sun et al. (1995), who reported that micelles in the aqueous phase act as an effective partitioning medium for hydrophobic organic compounds (HOCs); therefore, they reduce their affinity to sorb to soil. This was confirmed by the lower K_d values obtained in their study. Similarly, Chappell et al. (2005) investigated the effect of Brij 35 on the adsorption of atrazin and found that Brij 35 competes with atrazin for sorption sites in the soil and in the presence of micelles; it has the potential to dissolve atrazin.

The relation between the zero point of charge (zpc) and the sorption results is of interest in this study. Basically, the zpc for the soil was achieved at pH 3.4 and the pH of the tested soil solution was 5.7. This indicates that the soil surface will be negatively charged. Accordingly, the dominant form of MON is the anion form (Sassman and Lee, 2007). The reported Log K_{ow} for MON is 4.24 at pH 5 which is the highest calculated value compared to 2.75 at pH 7 and 3.79 at pH 9. Since the larger the log K_{ow}, the more hydrophobic the compound, it is expected that monensin with its lipophilic character will attract cations in soil such as Na^+ or k^+ and form the complexes by initiating a cation-organic anion complexation. This results in a neutral complex, increasing the sorption to soil. This explanation is in agreement with our results. They indicate that the higher affinity of monensin in the aqueous solution when compared to the soil water surfactant medium reflects the immobility of monensin in soil.

However, in the presence of the micelles of the nonionic surfactant, monensin exhibits low sorption potential to soil. There are two reasons for this. First, above zpc, more donor sites are available in soil. This in turn, increases the likelihood of forming hydrogen-bonding interactions between the soil surface and the surfactant micelles leading to a competition between Brij 35 and MON for binding sites. Secondly, the solubilization power of micelles is another factor. It is evident that surfactants are capable of promoting the apparent water solubility of contaminants through their solubilization in the micelles core (Edwards et al., 1991). Generally, above CMC, micelles are formed in a spherical shape orienting their hydrophilic ethelyne oxide groups (heads) to the exterior and their hydrophobic alkyl chains (tails) in the interior (Chiou et al., 1998). Therefore, it is expected that hydrophobic compounds are trapped inside the micelles cores. However, the hydrophilic compounds are solubilized in the neighborhood of the stern layer in the exterior (Katagi, 2008). Furthermore, the partitioning amount of MON in the solution is increasing in the presence of micelles, which can further enhance the release of higher concentrations of pre-sorbed MON. This conclusion matches the findings of Sun et al. (1995), Wang and Keller (2008) and ElSayed et al. (2013). Additionally, the pka values of the carboxyle group were significantly increased in the micelles of the nonionic surfactant Tween 80. Since the MON molecule contains several carboxyle groups in the backbone, it is expected that the pka value will rise inside the micelles leading to the presence of a negative charge that requires more cations to be neutralized. Accordingly, forming complexes are likely to occur, thus, increasing the hydrophobicity of MON.

On the other hand, the calculated K_F value in the presence of surfactant monomers is lower compared to the aqueous medium. Generally, when monomers are present in the solution at concentrations below CMC, the surfactant tends to sorb to soil in higher concentrations. As a consequence, higher amounts of the chemical are sorbed to the soil. This was indicated in several studies (Rodriguez-Cruz et al., 2004; Paria, 2008). However, in the present study, the low affinity of MON to sorb to soil can be explained by the fact that when the monomers occupy the sorption sites in soil, not all MON molecules find binding sites available; therefore, those remaining are partitioned within the solution. This competition effect in the presence of monomers is observed for some pesticides (Kile and Chiou, 1989; Edwards et al., 1991). The release of the pesticide, phenanthrene, from contaminated soils was increased primarily in the presence of alcohol ethoxylates surfactants such as Alfonic 810-60 and Novel II at concentrations below CMC (Aronstein et al., 1991). To date, very few studies have investigated the sorption of antibiotics in a soil-water surfactant system. Hari et al. (2005) indicated that, unlike acetaminophen and carbamazepine, nalidixic acid and norfloxacin exhibit low affinity to soil in the presence of the non-ionic surfactant NP9, indicating that the sorption behavior of the two groups of antibiotics is not ruled by their solubility or log K_{ow}. Therefore, it is clear that the sorption of antibiotics in the presence of surfactant is not predictable in terms of their hydrophobicity.

4.3.2 Mass balance

The mass balance for MON is presented in Table 4.4. For all irrigation treatments, MON concentrations were found to be below the detection limit by day 90. In both the water and surfactant-irrigated treatments, the total amount of MON detectable in the system (soil + leachate), declined from an initial (applied) level of about 10.40 mg to less than 0.20 mg after 30 days in the tap water irrigation. However, MON concentrations declined to reach 0.14 – 0.21 mg by day 60 for both irrigation treatments with surfactant. The relative amount of MON in the two lower soil layers (15-45 and 45-70 cm) to that in the upper layers (0-5 and 5-15 cm) was higher in the presence of surfactants in the first 21 days. This is expected as, apparently, no amount of MON was recovered from the layer (45-70 cm) in the absence of surfactant.

From 21 days onward, the total amount of recovered MON was greater in the surfactant treated columns than in those receiving tap water (Table 4.4). After 60 days, the total amount of MON detected in the surfactant treatment at the 5 g L^{-1} treatment was 1.5 times the amount detected in the treatment at 0.5 g L^{-1}. However, MON was under the detection limit in the tap water treatment. The percentage of unrecovered MON (Fig 4.3) varies for irrigation type up to 21 days. Subsequently, at day 22, the percentages of 93.36, 76.72 and 75.50 degraded from the initial concentration in the water treatment and surfactant treatments at 0.5 and 5.0 g L^{-1}, respectively. Overall, within 30 days, MON was under the detection limit in the tap water. This is consistent with the findings of Donoho, (1984) who stated that MON degraded in soil, with or without cattle manure, within a month from its application at 1 mg kg^{-1}. However, in the presence of Brij 35, MON still remained at low concentrations for 60 days.

Apparently, a greater amount of MON has been recovered in the presence of the nonionic surfactant Brij 35 compared to the tap water treatment. Despite the fact that MON is immobile in soil under 25 cm (Carlson and Mabury, 2006), in the present study, 0.26% of the applied MON was recovered in the leachate of the lysimeters irrigated with tap water, and 0.81 and 1.3%, respectively, for the 0.5 and 5.0 g L^{-1} surfactant solutions.. A similar study was conducted to calculate the mass balance of the antibiotic, oxytetracyline (OTC) in the absence and presence of Brij 35 at 0.5 and 5.0 g L^{-1} ; It was observed that a greater amount of oxytetracyline was detected in the leachate. Based on the initial amount applied to soil, the percentage of OTC found in the leachate was 6.47% and 3.86% in the treatment of Brij 35 at 0.5 and 5.0 g L^{-1}, respectively compared to 0.76% in the tap water (ElSayed et al., 2013). Although the percentages obtained for MON seem to be different, this may be due to the difference in the chemical structure and the degree of hydrophobicity between oxytetracyline and monensin.

The treatment differences in terms of the amount of unrecovered MON (Fig. 4.3) indicate a smaller amount of MON was recovered in the presence of the surfactant. This implies that the nonionic surfactant Brij35 could influence the degradation of MON in soil. Therefore, the half-life has been calculated for all treatments and found to be 5.72 days for the tap water treatment. Nevertheless, it increased to 9.62 and 11 days in the treatments with Brij 35 at 0.5 and 5.0 g L^{-1}, correspondingly. This indicates the persistence of MON in the presence of surfactants. Previous studies have reported the half-life to be 3.3 – 3.8 days in the field and 13.5 in the laboratory (Sassman, 2007; Carlson and Mabury, 2006). Our results are in agreement in the case of the half-life of MON in the tap water. However, our results for the surfactant treatments are quite different from that of the reported half-life in other studies. This reflects the effect of the presence of surfactants on the degradation of MON.

Abiotic degradation is a key factor in MON dissipation in soil (Sassman and Lee, 2007). However, Carlson and Mabury (2006) indicated that abiotic degradation of MON was not observed in their study. They attribute that to the lack of active sites of oxidation, reduction or dealkylation in the MON molecule; therefore, they suggest the presence of enzymes is essential to the breakdown of MON. Similarly, Yoshida et al. (2010) observed that increasing the organic matter content resulted in a decrease in the half-life and an increase in degradation. These studies point out the role of biodegradation of MON, which could explain the shorter half–life reported in the field compared to the laboratory.

Ultimately, it is evident from the literature that surfactant can accelerate the degradation process of pesticides as a result of increasing their bioavailability in the soil (Bardi et al., 2000). Similar conclusions have been reported for the non-ionic surfactants Brij 30 and Tween 80 (Zhu et al., 2010 and Zhang and Zhu, 2012). However, in the present study, the presence of the non-ionic surfactant Brij 35 reduced the dissipation of MON. This is consistent with the findings of Yoshioka and Stella (2002); they investigated the effect of surfactants on the degradation of Beta - Lactam antibiotics and reported that unlike anionic surfactants, the presence of the non- ionic surfactant Brij 35 (above CMC) showed an inhibition effect of the acid degradation of propicillin. They added, the more hydrophobic the surfactant, the more likely to suppress the degradation of the antibiotic. Furthermore, Mohammed-Ali (2012) observed that the stability of tetracycline in solution was higher in the presence of the non-ionic surfactant Tween-80. The author indicated that, tetracycline molecules could have been captured inside the micelles cores. This behavior could prevent them from forming the metabolite, anhydrotetracycline, and maintain their stability in solution. Recently, ElSayed et al. (2013) indicted that in sandy soil, degradation of oxytetracycline has been reduced in the presence of Brij 35 at concentrations above CMC.

4.3.3. Effect of Brij 35 on MON residues in soil

The downward movement of MON in sandy soil was assessed in the presence of Brij 35 in the irrigation water and compared with tap water irrigation. Figures 4.4, 4.5, 4.6 and 4.7 show the average concentrations of MON in soil over a ninety day period for topsoil at soil depths of 0.1, 0.3 and 0.6 m. The concentration of MON exhibits different trends depending on depth.

Generally, the highest concentrations were detected at the soil surface in all treatments and then decreased at lower depths. At the soil surface, the concentration decreased, confirming the increase in the degradation rate by time; the mean concentration right after application was 975.58, 971.92 and 950.60 µg kg^{-1} in the tap water, Brij 35 0.5 and Brij 35 5 g L^{-1}, respectively. At day 15, the concentration was reduced considerably in the tap water (148.25 µg kg^{-1}) when compared to both treatments with surfactant (301.47 and 286.41 µg kg^{-1}).

Table 4.4 Amounts of monensin (mg) in different soil profile depth ranges, cumulated in leachate, and overall, over a 63 day period. (— implies monensin was below detection levels)

Day	Irrigation solution Soil profile depth range (cm) / Cumulative leachate / Total ± *SD																	
	Tap water						Brij 35 @ 0.5 g L^{-1}						Brij 35 @ 5 g L^{-1}					
	0-5	5-15	15-45	45-70	Cum. leachate	Total	0-5	5-15	15-45	45-70	Cum. leachate	Total	0-5	5-15	15-45	45-70	Cum. leachate	Total
0	10.47	— Irrigation I —			0.00	10.47 ±0.08	10.43	— Irrigation I —			0.00	10.43 ±0.12	10.2	— Irrigation I —			0.00	10.25 ±0.45
1	4.75	0.05	0.0	—	0.01	4.8 ±0.35	4.52	0.05	0.12	0.05	0.05	4.80 ±0.11	3.62	0.11	0.08	0.10	0.05	3.97 ±0.21
5	3.23	0.07	0.00	—	0.01	3.32 ±0.18	4.14	0.11	0.08	0.12	0.05	4.51 ±0.23	3.07	0.12	0.08	0.10	0.05	3.41 ±0.18
15	1.59	0.03	0.009	—	0.01	1.63 ±0.19	3.23	0.07	0.09	0.08	0.05	3.53 ±0.31	4.71	0.08	0.06	0.08	0.05	3.35 ±0.22
21	—— Irrigation II ——				0.02	1.66 ±0.15	—— Irrigation II ——				0.08	3.62 ±0.30	—— Irrigation II ——				0.10	3.46 ±0.12
22	0.62	0.01	0.02	—	0.02	0.69 ±0.16	2.19	0.05	0.05	0.04	0.08	2.42 ±0.09	2.13	0.07	0.08	0.09	0.10	2.49 ±0.28
30	0.16	0.00	0.00	—	0.02	0.19 ±0.02	0.29	0.03	0.05	0.05	0.08	0.55 ±0.14	0.25	0.06	0.03	0.06	0.10	0. 52±0.12
42	—— Irrigation III ——				—	—	—— Irrigation III ——				0.08	0.64 ±0.06	—— Irrigation III ——				1.42	0.66 ±0.14
60	—	—	—	—	—	—	—	—	—	—	0.08	0.14 ± 0.02	—	—	—	—	1.42	0.21 ±0.03
63	—— Irrigation IV ——				—	—	—— Irrigation IV ——				—	—	—— Irrigation IV ——				—	—

* SD stands for standard deviation

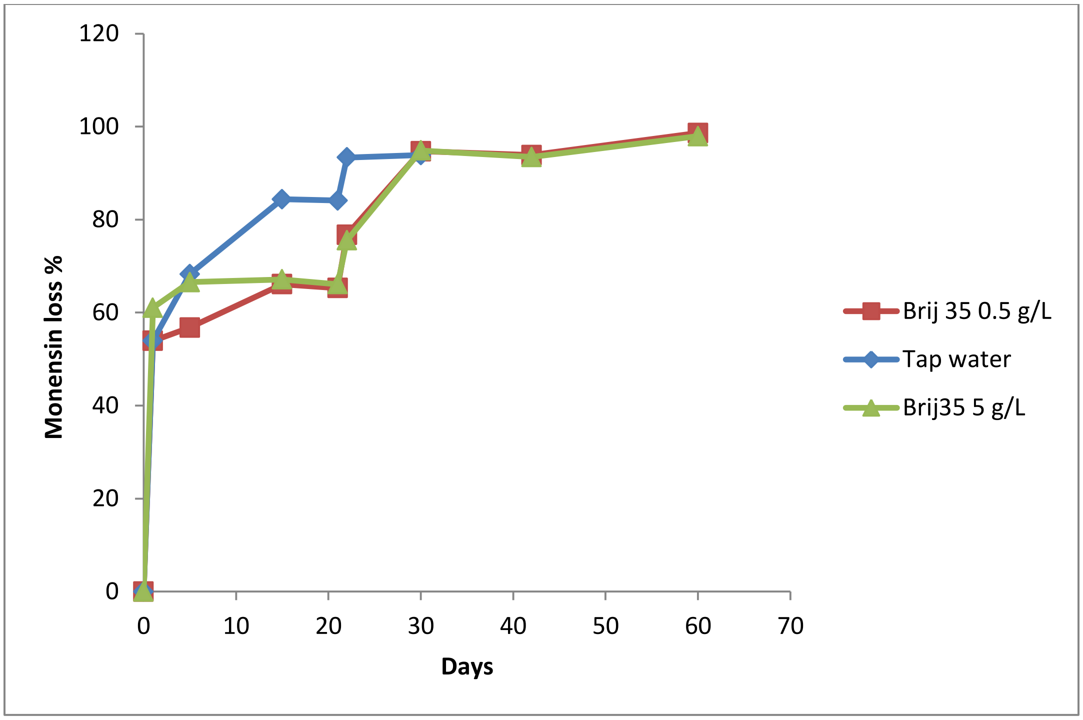


Figure 4.3 Monensin lost percentage in the season in the absence and presence of surfactant

At day 60, MON concentrations were under the detection limit in the tap water treatment. MON was found to be completely degraded within 3-4 weeks under field conditions and 78 mm irrigation water (Carlson and Maburay, 2006). However, our results showed that MON degraded over time to reach 5.48 and 6.60 µg kg^{-1} in the treatments of Brij 35 at 0.5 and 5 g L^{-1}, respectively.

At the 0.1m depth, higher concentrations of MON were detected in the surfactant treatments in the first 5 days followed by a gradual decrease (Fig. 4.5); however, concentrations in the tap water increased from day 1 to day 5 and then decreased noticeably by day 15 to be non-detectable by day 30. At a depth of 0.3 m, MON concentrations were found only in the treatments of surfactants with the exception of day 22; MON was detected in the tap water treatment at the low concentration of 0.52 µg kg^{-1}. Likewise, at the 0.6 m depth, MON concentrations (20 µg kg^{-1}) were detected in the surfactant treatment until day 30. The decrease in the concentrations of MON by time and depth indicates that MON moved downward in the soil while, at the same time, it degraded over the ninety day period. Such a decrease is considered as a significant effect ($P \leq 0.01$) of treatment, depth, time and interaction among these factors. Given that MON is strongly sorbed to soils, the enhanced mobility of MON in soil in the presence of surfactant as compared to tap water may be due to the interaction between soil and surfactant. As indicated earlier, the sorption of nonionic surfactants onto soil is an important factor and may result in competition between Brij 35 and MON for binding sites in the soil organic matter. The observed mobility of MON in the lysimeters from the surface to a 0.6 m depth can be clarified by the fact that Brij 35 is competing effectively with MON for sorption sites.

Since nonionic surfactants are known for their ability to desorb pesticides from soils, Mata Sandoval et al. (2000) reported that Triton X-100 showed a high efficiency to release pesticides from soil by replacing the pesticide on the sorption sites in soil. Yong and Mulligan (2004) suggested that the huge molecular size of certain compounds may allow them to effectively compete with other compounds for sorption sites in the soil. This could be applied to the present study due to the molecular size of Brij 35 (1199.55) compared to (690.72) for MON. Furthermore, the mobility of contaminants such as pesticides increased due to irrigation with wastewater, suggesting that surfactants in wastewater are the main factor affecting the leaching potential of pesticides (Muller et al., 2007). Likewise, non-ionic alcohol ethoxylates (AEs) at high concentrations are found to enhance the downward movement of pesticides in soil columns (Huggenberger et al., 1973).

4.3.4. Effect of surfactant on MON residues in water

Monensin concentrations in the leachate samples were measured in order to quantify the amount of MON leached in shallow ground water. The results indicated that higher concentrations of MON were detected in the leachate collected from the surfactant treatments.

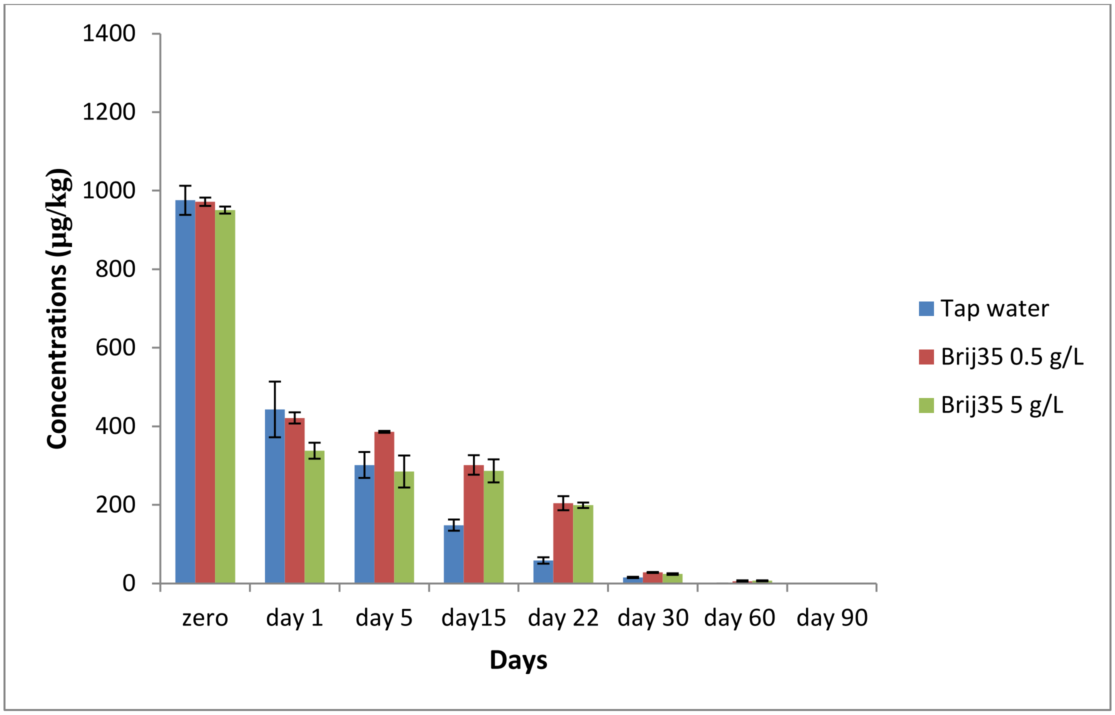


Figure 4.4 Monensin concentrations in the soil at the surface

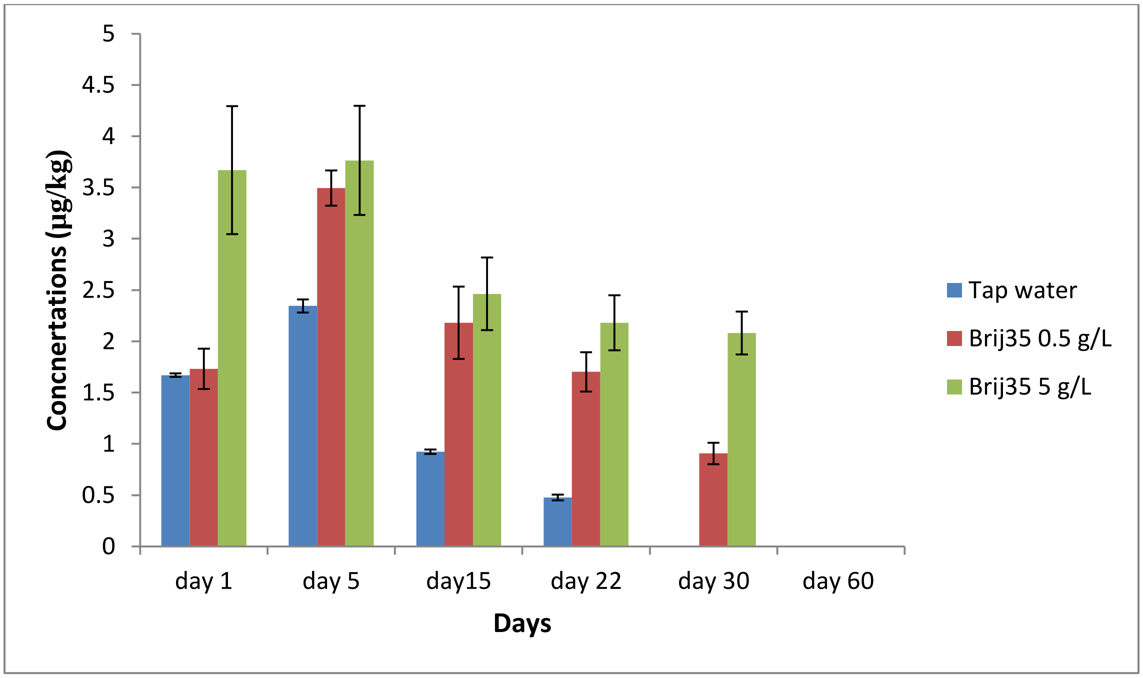


Figure 4.5 Monensin concentrations in the soil at 0.1 m depth

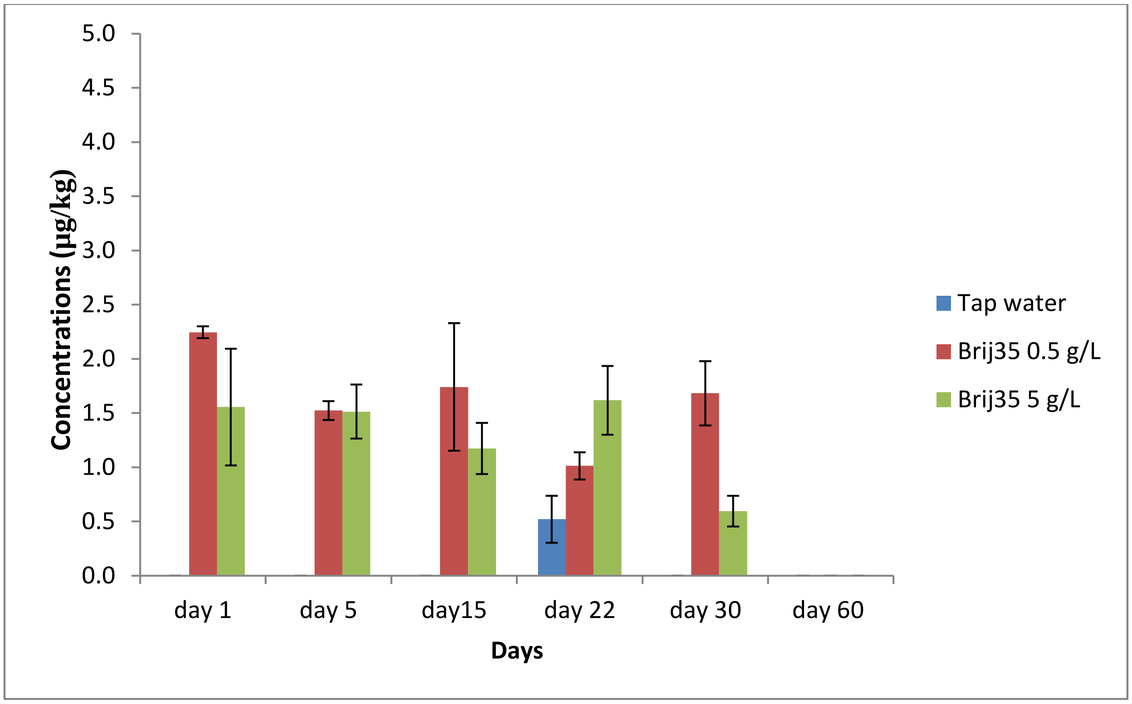


Figure 4.6 Monensin concentrations in the soil at 0.3 m depth

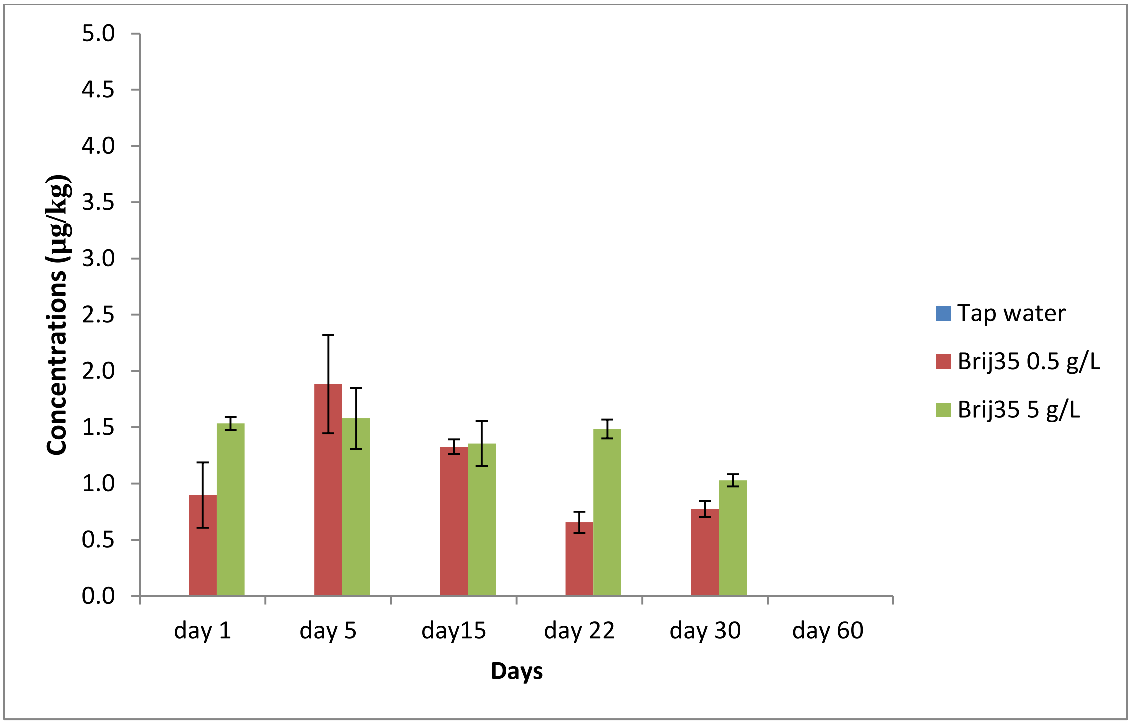


Figure 4.7 Monensin concentrations in the soil at 0.6 m depth

The maximum concentrations were measured after the first two irrigations in the treatment of Brij 35 at 0.5 L^{-1}; they become non-detectable after the third irrigation. In the case of Brij 35 at 5 g L^{-1}, MON concentrations were detected at the highest 5.13 and 4.92 µg L^{-1} after the first and the second irrigation events, respectively. This decreased to 3.63 µg L^{-1} after the third irrigation event (Fig 4.8). On the other hand, in the leachate of the tap water, MON concentrations were 1.53 and 1.40 at the first and second irrigations, respectively. Mon became non-detectable after the third application (38 days after the beginning of the season). These results could be attributed to less surface area and a very limited amount of silicate minerals in sandy soils in the lysimeter. This reduces the affinity of alcohol ethoxylates AEOs to sorb to soil (Krogh et al., 2003).

Furthermore, the application of manure is found to be a source of dissolved organic matter in the soil solution and this might enhance the mobility of antibiotics (Dolliver and Gupta, 2008; Aga et al., 2003; Thiele–Bruhn, 2003). This observation has been documented for several pesticides in soil (Graber et al., 2001; Worall et al., 1999). However, in a field study carried out by Carlson and Mabury (2006), the application of manure showed no influence on the mobility of three antibiotics namely, monensin, chlorotetracycline and tylosin. In the present study, the maximum concentration in the leachate (5.83 µg L^{-1}) was lower than the concentration of 40 µg L^{-1} in samples collected from the beef lagoon by Sassman (2007). However, this amount is about 4 times greater than detected in the surface water sample (1.2 µg L^{-1}) near agricultural areas (Hao et al., 2006; Lissemore et al., 2006).

Leaching of immobile antibiotics has been observed already; Kulshrestha et al. (2004) reported an increase in oxytetracycline mobility in clay soil as a result of competition between the antibiotic and humic acids for sorption sites in soil. Similarly, Chefetez et al. (2008) stated that the mobility of naproxen is observed in soil columns irrigated with secondary treated wastewater. They suggested that the competition between naproxen and the dissolved organic matter (DOM) in wastewater is a more likely reason for such mobility. Further, due to the ability of DOM to increase the apparent water solubility of MON, which results in lower sorption affinity, MON concentrations are detected in the leachate from lysimiters packed with silt soil amended with beef manure (Dolliver and Gupta, 2008). Recently, a lysimeter study indicated that the mobility of Oxytetracycline increased in soil columns irrigated with surfactant rich water (ElSayed et al., 2013).

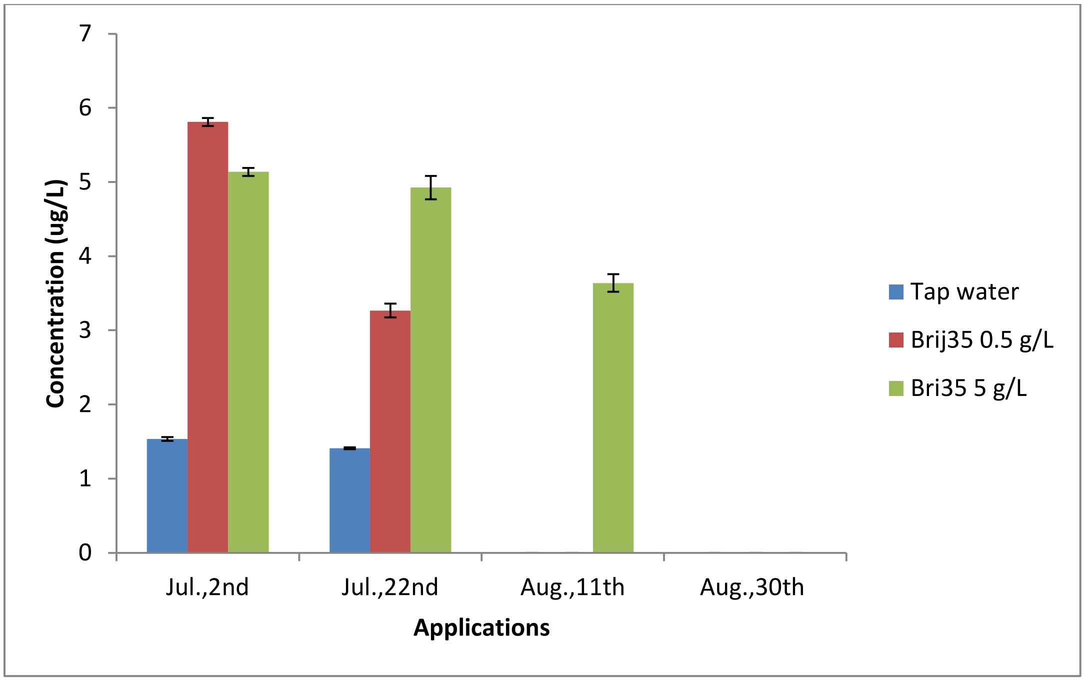


Figure 4.8 Monensin concentrations in the leachate

Fundamentally, the effect of surfactants varies based on the CMC concentration, chemical properties, the degree and the position of solubilization in the micelle. Therefore, in our study, when the concentration of Brij 35 was above CMC, the potential to form micelles was found to increase. Then, the lipophilic end (alkyl chain) of the surfactant molecule aggregates together inside the micelle, with the hydrophilic end point towards the aqueous phase on the exterior (Cheah et al., 1998). Due to this action, MON will be captured inside the micelle core and hence, exhibit weak sorption energy with soil.The significant amount of leached

MON in the treatment with both concentrations of Brij 35 could be due to the ability of Brij 35 to form micelles, which dissolve MON and increase its movement after each irrigation event. Additionally, several studies have been conducted to investigate the effect of surfactants on soil properties (Koren, 1972; Abou Zreig, 1999; Singh and Kumar, 2000). They concluded that nonionic surfactants increased soil dispersion leading to a greater leaching potential of contaminants. Likewise, Tao et al. (2006) reported an increase of the sorption sites in soil because of soil dispersion. Consequently, enhanced infiltration due to increasing water penetration is observed (Abou-Zreig, 2003; Katagi, 2008).

Collectively, above the CMC of a given surfactant, the apparent solubility of hydrophobic organic compounds is prone to increase significantly owing to solubilization. For example, the presence of the non-ionic surfactant, polyoxyethylene 20 sorbitan mono oleate was found to increase the apparent aqueous solubility of dodecane by six orders of magnitude (Pennell et al., 1993). Essentially, the ability of solubilizing polar compounds is observed to be positively related to the number of oxyethelyne groups (EO) in the molecule, which represents the hydrophilic character of the non-ionic surfactants (Xiarchos and Doulia, 2006). The greater the number of EO groups present in the exterior, the more hydrophilic the surfactant will be (Jafvert et al., 1994). Since Brij 35 has twenty-three (EO) groups, it is expected to exhibit a high capacity to solubilize polar compounds. Given the fact that the sorption of nonionic surfactants can affect the solubilization power, the findings of Krogh et al. (2003) can be of importance. They indicated that greater sorption was observed for alcohol ethoxylates AEOs with a lower number of ethylene oxide units (EOs) compared to those with longer EOs (Krogh et al., 2003). As stated ealier, Brij 35 has a long EOs (23 units); therefore, it could exhibit a low affinity to sorb to soil resulting in a higher number of micelles present in the solution. This will cause greater solubilization power and increase the mobility of hydrophobic compounds, such as MON.

Practically, the application of manure on a regular basis is considered the key input of antibiotics in soil. This leads to increased pH levels and results in greater ionization for such compounds. Basically, monensin as an ionophore contains carboxylic acid or ester groups in addition to tetrahydropyran or tetrahydrofuran groups in the backbone; these groups undergo different types of reactions in soil. Specifically, more than 99% of monensin is ionized at pH 7 and 9 (Sassman and Lee, 2007). At higher values of pH, the monensin molecule is neutralized by chelating with cations and forms complexes which are more likely to increase the log K_{ow} of the ionized monensin. This, in turn, increases the hydrophobicity and greater solubilization capability by nonionic surfactants can be expected.

Conclusions

Investigating the mobility of monensin in the soil-water-surfactant system is an essential step in evaluating the risk resulting from irrigation with surfactant rich water. The lysimeter experiments showed that the leaching potential of monensin increased in the presence of non-ionic surfactant at concentrations above CMC. This could be due to the encapsulation-like behavior of monensin, which results in the formation of complexes with cations in soil and leads to a more hydrophobic exterior. Therefore, it is more likely to be solubilized inside the lipophilic core of the micelles, which were formed at concentrations of Brij 35 above CMC. These results are supported by the sorption experiment showing that K_F values of monensin were significantly lower in the presence of the surfactant suggesting the lower sorption affinity to soil in the presence of the surfactant. Despite the fact that some studies reported monensin as immobile, our results indicated otherwise, and confirmed the enhanced mobility of monensin in the presence of the nonionic surfactant Brij 35.Therefore, the continuous use of surfactant rich water as an alternative to fresh water for irrigation can increase the potential for monensin to move downward in the soil profile and poses a risk for groundwater contamination. The present study also highlights the role played by the application of antibiotic contaminated manure in releasing these antibiotics into the environment.

Connecting Text to Chapter 5

As articulated in Chapters 3 and 4, the sorption of oxytetracycline and monensin to soil was investigated. Although both antibiotics belong to two different classes i.e. tetracycline antibiotics and ionophores, they are both reported as immobile in soil. Therefore, the effect of non-ionic surfactants on mobile antibiotics needs to be studied. Being mobile in soil and structurally quite different, sulfachloropyridazine was selected to compare with oxytetracycline sorption/desorption behaviour in the presence of the surfactant and to test the efficiency of the surfactant in desorbing these antibiotics from soil.

This chapter focuses on the sorption/desorption behavior of oxytetracycline and sulfachloropyridazine in a soil-water-surfactant-system. The sorption/desorption experiments and testing the efficiency coefficient of the surfactant were carried out under laboratory conditions. The results obtained from the study were partially interpreted in the context of the findings, reported in Chapter 3.

This chapter is a manuscript submitted for the Journal of Environmental Quality. The manuscript is co-authored by my supervisor, Dr. S. O. Prasher. The format of the original draft has been modified to remain consistent with the thesis format. All literature cited in this chapter are listed in the Bibliography (Chapter 9) at the end of the thesis.

Chapter 5 - Sorption/Desorption Behavior of Oxytetracycline and Sulfachloropyridazine in the Soil Water Surfactant System

Eman ElSayed and Shiv Prasher

Abstract

Sorption/desorption of antibiotics, oxytetracycline (OTC) and sulfachloropyridazine (SCP) was investigated in the presence of a nonionic surfactant Brij 35. Batch sorption experiments indicated that Freundlich equation fits sorption isotherms well for OTC. The sorption coefficients, $K_{F,}$ values were computed as 23.55 mL g^{-1} in the absence of Brij 35 and 25.46 mL g^{-1} in the presence of Brij 35 in the monomer form (below critical micelle concentration of 74 mg L^{-1}). However, the K_F values reduced to 12.76 mL g^{-1} in the presence of Brij35 at 2.5 g L^{-1}. Therefore, irrigation with surfactant-rich water may increase the leaching potential of OTC. In the case of SCP, the K_F value, in the absence of Brij 35, was 19.95 mL g^{-1}. As a result of increasing the concentration of Brij 35 to 0.25 g L^{-1} (about 2.5 CMC), K_F values first increased and reached a maximum value of 95.49 mL g^{-1} and then reduced to 66.06 mL g^{-1}, at surfactant concentration of 5 g L^{-1}. Unlike OTC, the presence of surfactant in irrigation water is likely to decrease SCP leaching. In the case of OTC, hysteresis was found at Brij 35 concentrations below CMC. However, OTC desorbed readily from soil (no hysteresis) at Brij 35 concentrations above CMC. In the case of SCP, no hysteresis was found in the presence of the surfactant, both below and above CMC. Further, the obtained values of the efficiency coefficient (E), reveals that Brij 35 had the potential to release more OTC from the soil ($E > 1$) as compared to SCP ($E < 1$). From these results, it can be concluded that regular use of manure on agricultural soils, especially in regions where poor quality irrigation water is used, can increase OTC contamination of water resources.

Key words: oxytetracycline, sulfachloropyridazine, non ionic surfactant, sorption, desorption

5.1 Introduction

Recently, the release of antimicrobial agents into the environment has become of great concern. Antibiotics are widely used to control disease in both humans and animals. Since antibiotics are designed to enter the body and to be excreted without metabolism, up to 90% of these antibiotics are released in animal feces as parent compounds (Halling-Sorensen et al., 1998). Due to their high consumption rate, considerable amounts may be released into the environment and contaminate water bodies. The risk increases in the presence of antibiotic resistant genes, which developed as a result of the occurrence of residues of antibiotics in different environmental matrices. Antibiotics can enter the ecosystem via two main sources: point sources, which refer to the discharge of municipal and industrial wastewater, and non-point sources which include runoff from agricultural fields or from spreading sewage sludge and from leaching in agricultural soils. Spreading manure as a fertilizer is a common practice. It is one of the non-point sources that introduces antibiotics into soils and groundwater and thus, leads to water quality impairment (Hamscher et al., 2005).

Antibiotics are large molecules that are pH dependent and they can form complexes with soils. They can be more persistent in the environment due to their high polarity. Oxytetracycline and sulfachloropyridazine represent two major groups of antibiotics. They are used extensively in human medicine and in concentrated animal feed operations (CAFO) as medication and as a growth promoter. Oxytetracycline (OTC) has been detected in manure in concentrations as high as 29µg g^{-1} as was reported by Martinez-Carballo at al. (2007). Similarly, tetracyclines have been detected in manure samples at a concentration of 46 µg g^{-1} (Uslu and Balcioglu, 2009). Another antibiotic, Sulfachloropyridazine (SCP), one of the sulfonamides, represents 2.3% of all antibiotics used in the United States. Sulfonamides are designed to interrupt the bacterial synthesis of folic acid; it is vital for the synthesis of bacterial DNA. Therefore, they have a bacteriostatic effect that allows them to limit bacterial growth. SCP has been detected in several constituents, notably, in soil at concentrations of 1.55 mg kg^{-1} (Boxall et al., 2002) and up to 365 mg kg^{-1} (Kay et al., 2005). However, in manure, it has been detected at concentrations of 91 mg kg^{-1} (Martinez-Carballo et al., 2007).

Studies have shown that the sorption of antibiotics in soil systems can be influenced by various mechanisms, such as electrostatic interaction, complexation with metals or forming cation bridging and hydrophobic partitioning (Boxall et al., 2002; Figueroa-Diva et al., 2010; TerLaak et al., 2006; Tolls, 2001; Vasudevan et al., 2009). OTC is known for its high affinity to sorb to soil and clay. It has the ability to chelate with inorganic minerals, monovalent and multivalent cations in soil organic matter and to form metal complexes. Therefore, OTC is categorized as immobile in soil (Sithole and Guy, 1987; Mackay and Canterbury, 2005). The sorption coefficient (K_d) values of OTC are reported to be between 416 and 1026 L/kg in sandy and sandy loam soil, respectively (Rabolle and Spliid, 2000). As a result of increasing pH and ionic strength, the sorption of OTC decreases in clay loam and loam sand soil (Terlaak et al., 2006). Likewise, Kulsherstha et al. (2004) observed that as dissolved organic matter (DOM) increases, the sorption affinity to soil decreases, leading to the enhanced leaching potential of OTC in soil. The sulfanomide distribution coefficient (K_d) in soil has been found to range from 0.9 to 3.5 indicating their high mobility through the soil profile which has been reported under field conditions (Boxall et al., 2002). Further, Thiele-Bruhn et al. (2005) showed that soil pH and the properties of soil organic colloids are important factors in determining the strength of sulfonamides sorption on soil.

Wastewater effluent is considered as a point source for many pollutants in the environment. Surfactants have been detected at the highest concentrations among the organic chemicals found in wastewater and sludge (Brunner et al., 1988; Field et al., 1992; Wild et al., 1990). Non-ionic surfactant concentrations ranging from 102-103 mg L-1 have been detected in wastewater (Narkis and Ben-David, 1985). As a result of the extensive use of non-ionic surfactants, such as alchohol ethoxylates (AEO) and alkylphenol ethoxylate (APEO), to remove skin grease in the leather industry, non-ionic surfactants were reported to be the major pollutants in untreated wastewater samples from the textile industries (Castillo et al., 1999). Surfactants are amphiphilic molecules consisting of a hydrophilic head and a hydrophobic tail. The hydrophobic group contains a long alkyl chain and the hydrophobic head consists of a certain number of ethylene oxide groups EO, which can be charged (anionic and cationic surfactants) or without charge such as non-ionic surfactants. At the critical micelle concentration (CMC), surfactants tend to aggregate together and form micelles.

In the treatment of effluents in wastewater treatment plants (WWTPs), surfactants undergo degradation to metabolites such as nonylphenol ethoxylates (NPEOs). Loyo-Rosales et al. (2007) indicated that these metabolites are not sufficiently eliminated by WWTPs and thus, they can be released into surface water. Ahel et al. (1996) reported that nonylphenols were detected at relatively high concentrations from 1.8 to 25 g L^{-1} in two rivers in Switzerland and up to 7.2 g L^{-1} detected in a pumping station for drinking water supply near these rivers. Studies show that many household products and detergents contribute to the considerable amount of these contaminants in urban sewers (Conn et al., 2006; Loyo-Rosales et al., 2007; Stuart et al., 2012). Further, the surfactant byproducts such as NPEO and nonylphenol (NP) are estrogen disrupting compounds that may pose a risk to aquatic organisms. In addition, the presence of non-ionic surfactants in irrigation water could enhance the mobility of chemicals in soils and result in the contamination of groundwater (Huggenberger et al., 1973; Kan and Tomson, 1990; Aronstein et al., 1991; Rodriguez-Cruz et al., 2004). For example, the mobility of the herbicide metolachlor in soil wasreduced in the presence of non-ionic surfactants at low concentrations (0.04 g kg^{-1}); however, by increasing the concentrations from 5- 50 g kg^{-1}, the mobility increased (Sanchez-Camazano et al., 1995). The release of the herbicide atrazine from soil is enhanced when the concentration of the nonionic surfactant, Brij 35, is increased in the solution (Chappell et al., 2005). They concluded that the more the formation of admicells on the clay surface, the greater the amount of atrazine released in the solution.

Furthermore, Katagi (2008) reported that at high concentrations of surfactants, an increase in the mobility of pesticides was observed in leached water.

Surfactants are also introduced into soil through the use of surfactant rich wastewater (i.e. grey water originating from household laundry effluent) as an alternative to fresh water for irrigation and consequently, it may increase the risk of water repellence in soil (Wiel-Shafran et al., 2006). Given the scarcity of water in many parts of the world, the reuse of wastewater has become an essential alternative option for irrigation. In arid and semi-arid areas, sometimes wastewater is used to irrigate crops and vegetables; this wastewater may be untreated, or partially treated, or both. Chatterjee (2008) indicated that untreated or primary treated wastewater is used in developing countries to irrigate land in order to cope with the food demand due to the growing population. Therefore, applying surfactant rich water as an alternative to fresh water can increase the amount of surfactants in soil and hence, could influence the fate of other chemicals that are applied frequently on regular basis to secure crop production. This in turn may have an impact on agricultural land pollution and environmental sustainability (Lehrsch and Sojka, 2011 and Wiel-Shafran et al., 2006).

Due to their different physico-chemical properties, oxytetracycline and sulfachloropyridazine, antibiotics from different functional groups, were chosen in this study to better understand their behavior in soil. The desorption process has essential environmental effects on the movement of chemicals in an aqueous medium. Thus, it is worthwhile to study the sorption and desorption behavior of these commonly used antibiotics when they are present with non-ionic surfactants in solution. To provide further information on their persistence in the environment, desorption hysteresis has been employed. To the best of the author's knowledge, no study has been conducted to investigate the sorption - desorption behavior of OTC and SCP in the soil water surfactant system. Therefore, the objective of this study was to investigate the sorption–desorption interactions of oxytetracycline and sulfachloropyridazine in the presence of the nonionic surfactant, Brij 35, as well as evaluating the desorption efficiency of Brij 35 of the above-mentioned antibiotics from soil.

5.2. Materials and methods

5.2.1. Study compounds

Oxytetracycline hydrochloride (OTC) 95% HPLC grade from Sigma-Aldrich, solubility 1g L^{-1} (Table 5.1). Sulfachloropyridazine (SCP) was purchased from Sigma-Aldrich (Table 5.1). The non-ionic surfactant Brij 35 [Polyoxyethylene lauryl ether $(C_2H_4O)_{23}$-$C_{12}H_{25}OH$] with critical micellar concentration (CMC) = 74 mg L^{-1} and HPLC-grade methanol and acetonitrile were obtained from Sigma-Aldrich. Mobile phase chemicals were purchased from Fisher Scientific. Double–deionized water (Milli-Q, Millipore, Molsheim, France) was used in the preparation of standard solutions and mobile phase solutions.

5.2.2. Soil characteristics

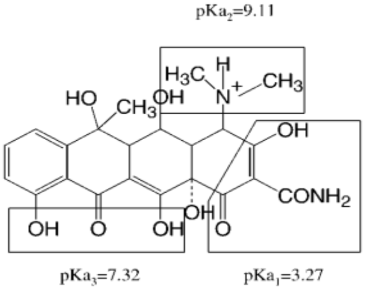
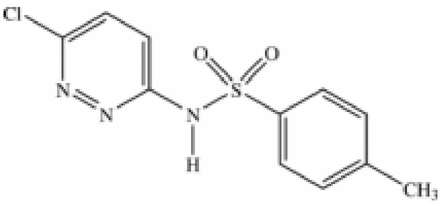
Belonging to the St. Amable complex, the sandy soil used was obtained from a field in the Macdonald Campus of McGill University, Ste-Anne-De-Bellevue, QC. Physical and chemical properties of the soil are given in Table 5.2.

5.2.3. Batch adsorption experiment

5.2.3.1. Antibiotic partitioning within soil water surfactant system

Adsorption of OTC onto soil in the presence of the nonionic surfactant Brij 35 was investigated through a soil equilibrium technique. Triplicate soil samples (1 g) were equilibrated with an aqueous solution (20 mL) of OTC at concentrations ranged from 5 to 50 µg mL^{-1} in factorial combination with Brij 35 concentrations of 0, 0.02, 0.25, 0.5 and 5 g L^{-1}. All solutions contained 0.01 M $CaCl_2$ to mimic the ionic strength of groundwater (Wilde et al., 2008). The soil slurry was placed in a 50 mL centrifuge tube, and placed on a shaker, for 48 hrs. The slurry was centrifuged at 2683 g for 20 min. Extraction and analysis of OTC proceeded, as described above. The proportion of OTC adsorbed was calculated by taking the difference between the amount initially present in solution and the amount remaining in solution after equilibrium with the soil.

Table 5.1 Physical and chemical characteristics of OTC and SCP

Antibiotic	Physical - chemical properties	Chemical structure
Oxytetracycline	Solubility : 1 g/L MW : 460.44 Log K_{ow} : -1.22[a] GUS index : -0.91[b] Pka1 : 3.27 [c] Pka2 : 7.32 pKa3 : 9.11	
Sulfachloropyridazine	Solubility : 7 g/L [d] MW : 284.72 Log K_{ow} : 0.31 pka : 5.5	

[a] Loke et al. (2002)
[b] PPDB (2009)
[c] Sassman and Lee (2005)
[d] Terlaak et al. (2006)

5.2.3.2. Influence of surfactant concentration in the antibiotics desorption

To investigate the desorption behaviour of OTC and SCP in an aqueous medium, desorption isotherms were obtained in triplicate from 1g soil samples initially treated with the solutions of OTC and SCP separately at concentrations ranging from 5 to 50 µg mL^{-1}. The soil samples were shaken for 48 hours. The slurry was centrifuged at 2683 g for 20 min. and the amount adsorbed to soil for each antibiotic was then determined. Afterwards, 10 mL of adsorption equilibrium solution was removed from the supernatant and immediately replaced by 10 mL of water. The samples were placed in suspension again and shaken for 48 hours. They were finally centrifuged at 2683 g for 20 min. then the antibiotic concentrations in the equilibrium solution were determined. To obtain desorption isotherms of OTC and SCP in a water surfactant medium, the same method as that employed to obtain the desorption isotherms in aqueous medium was used, except for replacing the 10 mL of the adsorption equilibrium solution with 10 mL of the surfactant solution at the tested concentrations.

Table 5.2 Physical and Chemical Characteristics of Soil

Soil Type	Sand (%)	Silt (%)	pH	Bulk Density (Mg m^{-3})	Organic Matter (%)	CEC (cmol kg^{-1})	Hydraulic Conductivity (cm d^{-1})	Zero point of charge (zpc)
Sand	92.2	4.3	5.5	1.350	2.97	4.9	1.67 (*S.D. = 0.45)	3.4

* S.D. stands for standard deviation

5.2.4. Analytical procedure

The soil samples and leachate were analyzed by HPLC with diode array detection DAD using eclipse plus C18 column (4.6 x 150 mm) from Agilent, USA. The mobile phase for OTC was 15% acetonitril and 85% of water containing phosphate buffer at pH 2.5 while it was 30% acetonitril and 70% of water containing phosphate buffer at pH 3.1. The flow rate was 1 mL/min and detection wavelength was at 355 nm for OTC and 270 nm for SCP with detection limit of 0.1 and 2 ng g^{-1} for OTC and SCP, respectively.

5.2.5. Sorption modelling isotherms

Freundlich type

The nonlinear form of the Freundlich adsorption model is represented by where q is the equilibrium capacity (mg of compound adsorbed kg^{-1} of soil), “C_{aq}” is the equilibrium aqueous-phase concentration (mg L^{-1}), K_F is the Freundlich sorption coefficient, and 1/n is the Freundlich measure of nonlinearity (Eq. 5.1).

$$q = K_F \, C_{aq}^{1/n} \qquad \text{Eq. 5.1}$$

The linearized form of the Freundlich isotherm can be written as

$$\mathrm{Log}\ q = \mathrm{Log}\ K_F + (1/n)\ \mathrm{Log}\ C_{aq} \qquad \text{Eq. 5.2}$$

Where

q is the amount of OTC sorbed (μg g^{-1}),

C_{aq} is OTC concentration after equilibrium in mg L^{-1}, and

K_F , $1/n$ are the Freundlich affinity and nonlinearity coefficients, respectively (L g^{-1})

Langmuir type

$$q = bK_L C_{aq} \,/\, \left(1 + K_L\, C_{aq}\right) \qquad \text{Eq. 5.3}$$

Where

b indicates the maximum achievable surface concentration of a given compound (μg g^{-1}), and

K_L is Langmuir sorption coefficient expressing binding energy (mL g^{-1}).

As a measure of sorption hysteresis, the thermodynamic index of irreversibility (TII) was calculated. Fundamentally, “TII” (Eq. 5.4) used as an indicator of the no singularity of the sorption–desorption isotherms. The index 0 indicates completely reversible systems and 1 for the approaching of the complete irreversibility (Sander et al., 2005).

$$TII = 1 - \left(\frac{n_d}{n_s}\right) \qquad \text{Eq. 5.4}$$

Where

n_s and n_d are the nonlinearity coefficients for sorption and desorption, respectively.

In order to calculate the efficiency coefficient (E), the following equation was employed (Eq. 5.5) to better determine the concentration of Brij 35 which enhances desorption of the antibiotics from soil

$$E = \frac{(1-D_S)}{(1-D_W)} \qquad \text{Eq. 5.5}$$

Where

D_s is the fraction of the chemical remaining sorbed in the presence of the surfactant, and

D_w is the fraction of the chemical remaining sorbed in the absence of the surfactant, relative to the initial amount sorbed.

$E > 1$ indicates enhanced chemical desorption and $E < 1$ shows inhibited chemical desorption. Data was analyzed with the aid of PROC GLM and Tukey in SAS v. 9.2 (SAS Institute Inc., 2010).

5.3. Results and discussion

5.3.1. Antibiotic partitioning within soil water surfactant system

Sorption plays a significant role in the factors affecting the transport of chemicals in soil. Therefore, this sorption experiment in the presence and in the absence of Brij 35 was carried out. The sorption isotherms of SCP in Bij35 solutions at concentrations (0, 0.02, 0.25, 2.5 and 5 g L^{-1}) are demonstrated in (Fig. 5.1). Sorption isotherms obtained for SCP fit the Langmuir model Eq. 5.3, with R^2 values between 0.87 and 0.99. However, R^2 values were less (0.60-0.95) when the Freundlich model was employed in modelling the same data Eq. 5.1, although this indicates a lesser fit when compared to the Langmuir model, K_F values increased in the same fashion as observed with Langmuir. Furthermore, n values which are presented in Table 5.3 indicate a Freundlich constant $n < 1$.The sorption nonlinearity showed a declining trend from 0.97 in the absence of the surfactant to 0.93 in the presence of surfactant monomers; this dropped noticeably to 0.50 in the presence of surfactant micelles. These different n values indicated slightly larger sorption heterogeneity in the presence of surfactant compared to sorption in the absence of surfactant.

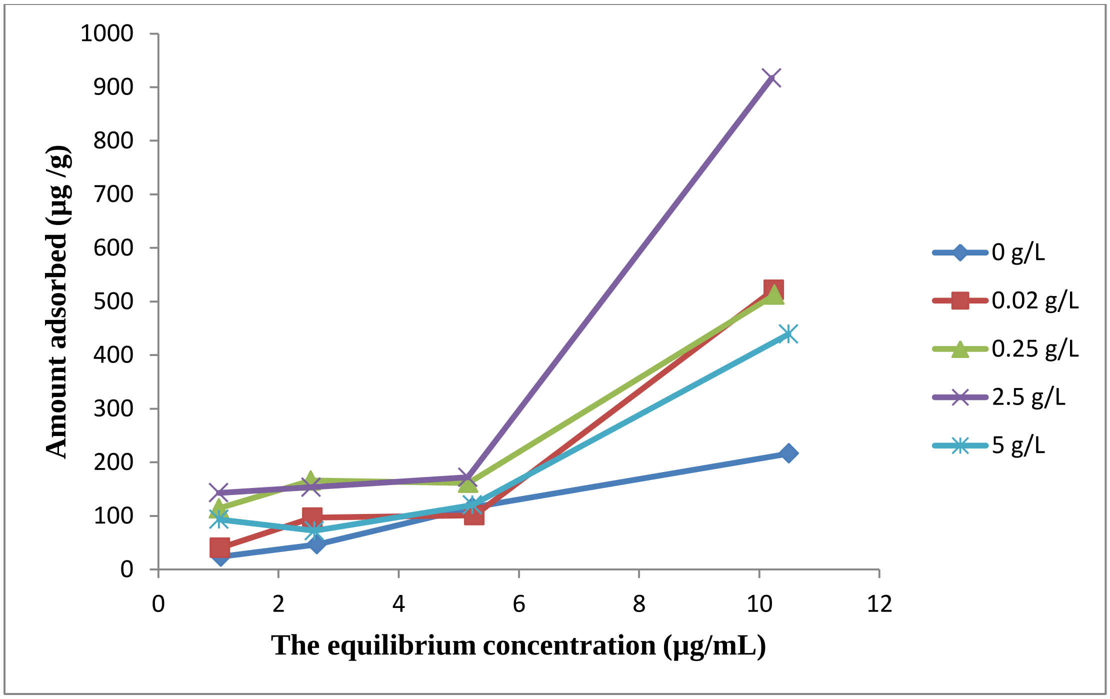


Figure 5.1 Sorption isotherms of SCP in the absence and presence of the non-ionic surfactant Brij 35

In terms of the value of the Langmuir (K_L) and Freundlich (K_F) sorption coefficients, they are found to be increasing by increasing the surfactant concentration from 0.02 – 2.5 g L^{-1} with respect to their values in the absence of surfactants (except for the drop of K_L and K_F values at 5 g L^{-1}) .The obtained values of K_L and K_F in the absence of Brij 35, show the lowest value (0.02 and 19.95), respectively. As a result of increasing the concentration of Brij 35 to 0.25 g L^{-1} (about 2.5 CMC), the K_L and K_F values increased to reach the maximum (0.85 and 95.49) and by increasing the surfactant concentration to 5 g L^{-1}, a decline in the K_L and K_F values (0.17 and 66.06) was observed.

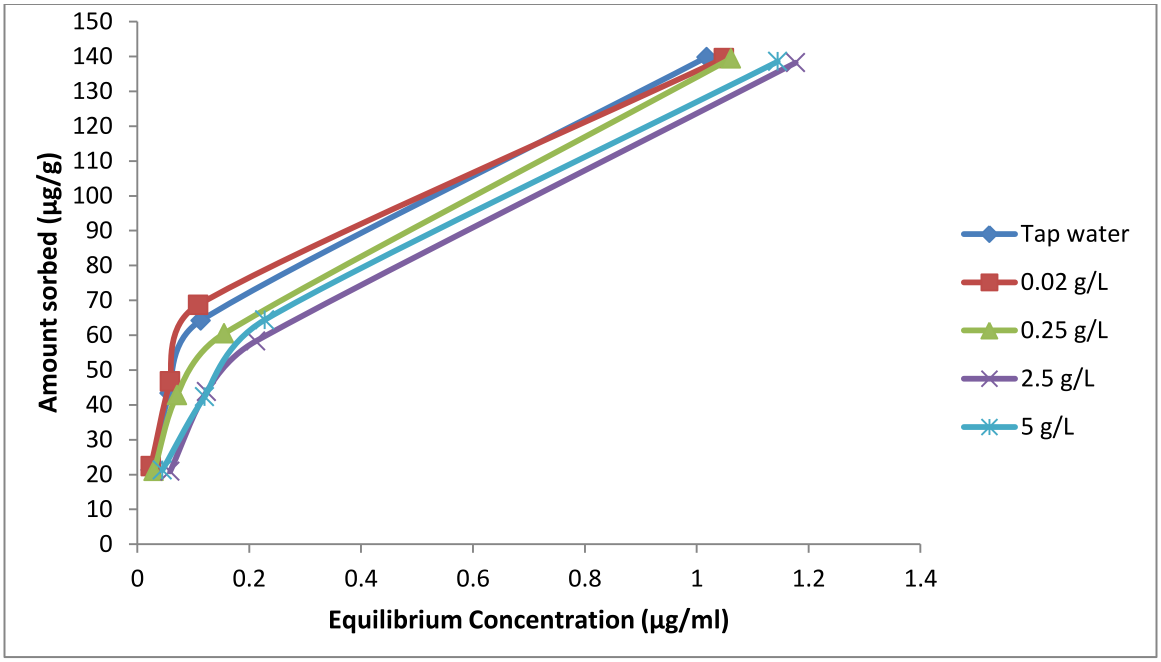


Figure 5.2 Oxytetracycline isotherms in the absence and presence of the non-ionic surfactant Brij 35 (ElSayed et al. 2013)

In the case of OTC, the sorption isotherms of OTC in Bij35 solutions at concentrations (0, 0.02, 0.25, 2.5 and 5 g L^{-1}) are demonstrated in (Fig. 5.2). Although OTC is water soluble, it shows high affinity to sorb to soil due to the formation of metal complexes with cations in the organic matter in soil. Jones et al. (2005) studied the Freundlich sorption coefficients (K_F) of OTC in different types of soil and found that soil texture, cation exchange capacity, and iron oxide content combined with the organic matter content are the main factors influencing OTC sorption. ElSayed et al. (2013) showed that Freundlich (K_F) sorption coefficients values were 23.55 mg mL^{-1} in the absence of Brij 35 then slightly increased to 25.46 in the presence of Brij 35 in the monomers form (below CMC). However, K_F values were reduced to 12.76 in the presence of Brij 35 at 2.5 g L^{-1}. They suggested that at the pH soil solution (pH = 5.7) where it exceeded the zero point of charge for the tested soil (pH = 3.4), the zwitterionic OTC^{0-+} will be dominant and hence sorbed to soil by either electrostatic attraction or hydrogen bonding. However, under the same experiment conditions and in the presence of Brij 35 above CMC, more sorption sites will be available. Thus, significant interaction mainly by hydrogen bonding is took place leading to a competition between the micelles and OTC. Therefore, low sorption coefficients of OTC in the soil water surfactant system were observed. This proves the effect of micelles in the sorption process of OTC because in the presence of monomers, high sorption affinity to soil was obtained. These results for OTC are obviously different compared to those obtained for SCP. Despite the fact that SCP is mobile in soil and exhibit low sorption affinity to soil (Boxall et al., 2002), in the present study, SCP sorption increased when Brij 35 was present in the solution in both the monomer and micelle forms. This could be attributed to the difference in the chemical characteristics of both antibiotics.

Table 5.3 Freundlich (K_F) and langumir (K_L) sorption coefficients of SCP in the presence of Brij 35

Brij 35 Conc. (g L^{-1})	K_F	n	b	K_L
0 (Tap water)	19.95	0.97	2.78	0.017
0.02	41.68	0.93	0.027	0.72
0.25	95.49	0.59	0.027	0.85
2.5	91.20	0.66	0.015	0.73
5	66.06	0.5	0.14	0.17

Given the fact that surfactants are amphiphilic compounds; they sorb to soil after application and this may provide an explanation for the observed high affinity of SCP sorption to soil in the presence of surfactant. The sorption of non-ionic surfactants onto soil has been studied (Kuhnt, 1993; Beigel et al., 1998; Shen and Yen, 1999; Shen, 2000; Paria, 2008). Since Brij 35 is a non-ionic surfactant and sulfonamides are amphoteric in nature and subject to protonation, it is assumed that SCP is zwiterionic (in the neutral form) having both a positive and a negative charge; it could be sorbed to Brij 35 (via hydrogen bonding) which already sorbed to soil and prevented SCP from existing in the solution. Furthermore, in our study, the pH of the soil solution is 5.7 and since pka = 5.5, it suggested that neutral SCP^{0-+} will be dominant. Terlaak et al. (2006) reported that SCP^0 is less water soluble than the anion SCP^{--} and hence, exhibits higher hydrophobicity resulting in higher affinity to the sorbed surfactant by hydrophobic interaction. This is consistent with the findings of Hari et al. (2005); they conclude that antibiotics with lower solubility and higher hydrophobicity strongly react with the adsorbed layers of surfactants.

These findings are in agreement with Boxall et al. (2006) who reported that under neutral or slightly acidic conditions, sulfonamides will exist in the neutral form. They can partition into the soil organic carbon and potentially reduce their mobility. Furthermore, significant changes in sulfanomides K_d values were observed as a result of rapid dissociation of sulfonamides with pH. Given that applying surfactant rich grey water changes the pH of soil and makes it more alkaline, it is possible that at higher pH values (pH 5-11), the dissociation of a proton from the sulfonamide group ($-SO_2NH-$) is occurring. It is assumed that binding with the positively charged sites in soil could take place, presumably by hydrophobic partitioning such as Van der Waals or cation exchange forces (Schwarz et al., 2012). Therefore, when more sorption sites are unavailable, surfactants as large molecules, could help provide more sorption sites via hydrogen bonds and dipole-dipole interactions for SCP and thus, reduce its concentration in the solution.

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5.3.2. Influence of surfactant concentration in the antibiotics desorption

Overall, these isotherms fit the Freundlich equation ($R^2 = 0.80$) for SCP and OTC (Fig. 5.3 and 5.4, respectively). The values of the desorption coefficient K_{Fd} decreased with respect to those of water in the desorption of the two antibiotics from soil except for SCP where the K_{Fd} value increased at Brij 35 concentration of 0.25 g L^{-1} with respect to those corresponding value in the aqueous medium.

The observed decrease in K_{Fd} in the desorption in water surfactant medium with respect to the values corresponding to desorption in water may result from the greater percentage of antibiotic desorbed compared to that corresponding to water. Therefore, the calculated value of the efficiency coefficient (E) (i.e. the ratio between the percentages of antibiotic desorbed in water-surfactant medium and in aqueous medium) was greater than 1 for OTC and less than one for SCP. However, this does not apply when the surfactant present in the solution is in the monomeric form (below CMC). The values of E varied for both antibiotics at the same surfactant concentration of 0.02 g L^{-1} and were found to be 1.06 and 0.94 for OTC and SCP, respectively. This indicates the desorption effect of surfactant monomers resulted in the higher E value for OTC while in the case of SCP, monomers have no effect and therefore, the E value was less than 1. Additionally, the observed difference in the desorption of SCP with respect to desorption in water are probably due to the decrease in the amount of surfactant in solution, originating from its adsorption by the soil. Moreover, it seems that SCP present in the soil-surfactant-water medium has been adsorbed by the lipophilic moiety of the surfactant which previously was adsorbed by the soil. Thus, there was a decreased SCP concentration in the surfactant solution when compared to the aqueous solution.

Desorption isotherms of OTC pre-adsorbed by soils in the presence and absence of surfactant were also obtained (Fig 5.3). The isotherms fit well the Freundlich equation. The values of the desorption constants (K_{Fd} and n_{Fd}) and the hysteresis coefficients represented as the thermodynamic index of irreversibility TII (Table 5.4) which decreased in the presence of the surfactant micelles. However, these values increased in the absence of surfactant and in the presence of surfactant monomers. Additionally, these treatments showed strong hysteresis (indicating the increased difficulty of the sorbed OTC to desorb from the matrix) compared to the treatment in the presence of surfactant micelles where weak hysteresis was observed. Fundamentally, the same observation was revealed in the case of SCP as no hysteresis was observed in the desorption of SCP with small range of TII values at all tested surfactant concentrations. Therefore, the hysteresis trend remains consistent in all the surfactant treatments except for the treatment at the highest concentration of 5 g L^{-1}, where slightly higher TII value (0.27) was observed. These findings are in agreement with Huang and Weber (1997) who reported that the degree of hysteresis is inversely related to the linearity of the sorption branch. This is true in our study as hysteresis increased in the presence of micelles in the solutions where n_{fd} decreased noticeably (Table 5.4).

The results show that the percentage of OTC desorption in the experiments carried out in a water-surfactant medium is greater than the desorption of OTC in water with E values higher than 1 (Table 5.4). These E coefficient values significantly vary in the range of 1.06-1.30 with the lowest effect obtained in the treatment of the monomer form. However, E values for SCP were in the range of (0.94 - 0.99) indicating that Brij 35 exhibits higher desorption ability to OTC compared to SCP. This may be attributed to the nature of the chemical structure of each antibiotic since the surfactant treatment was identical for both antibiotics. Furthermore, the results show that OTC is desorbed from the soil at all tested concentrations of Brij 35. This desorption is not affected by the decrease in Brij 35 concentration below CMC. As a matter fact, desorption of hydrophobic compounds such as pesticides (with greater K_{ow}) from soils by the surfactants in the monomeric form is documented (Kile and Chiou, 1989 and Edwards et al., 1992).

This conclusion was not observed in the present study since OTC with lower log K_{ow} (-1.22) was desorbed from soil in the presence of the monomers when compared to SCP log K_{ow} (0.31). This could be due to the fact that antibiotics are ionizable compounds and pH dependent so their sorption behavior is expected to be different than that of pesticides.

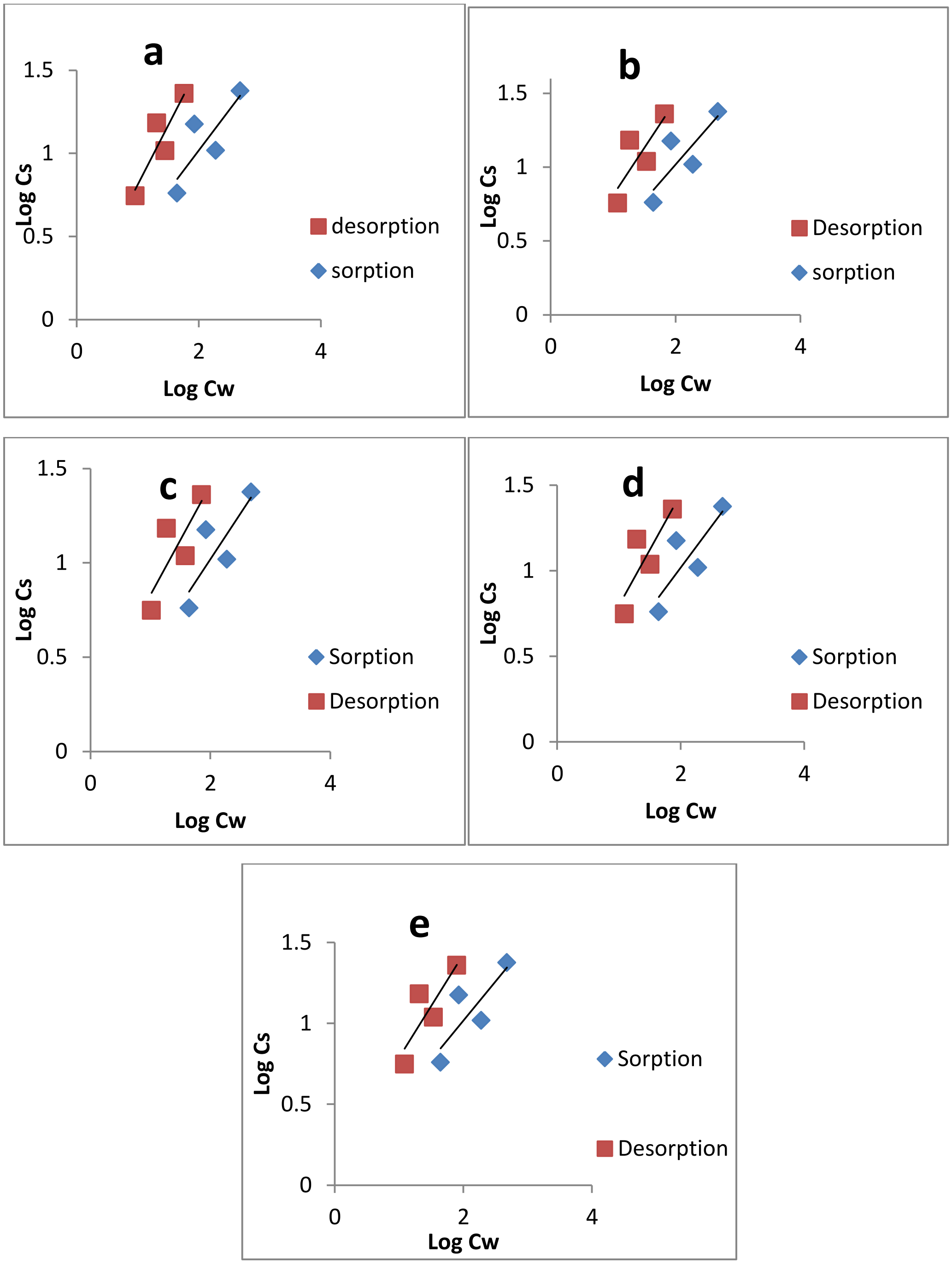

Figure 5.3 Desorption isotherms of SCP by Brij 35: a, b, c, d, e in the presence of Brij 35 at 0, 0.02, 0.5, 2.5, 5 g L^{-1} concentrations, respectively.

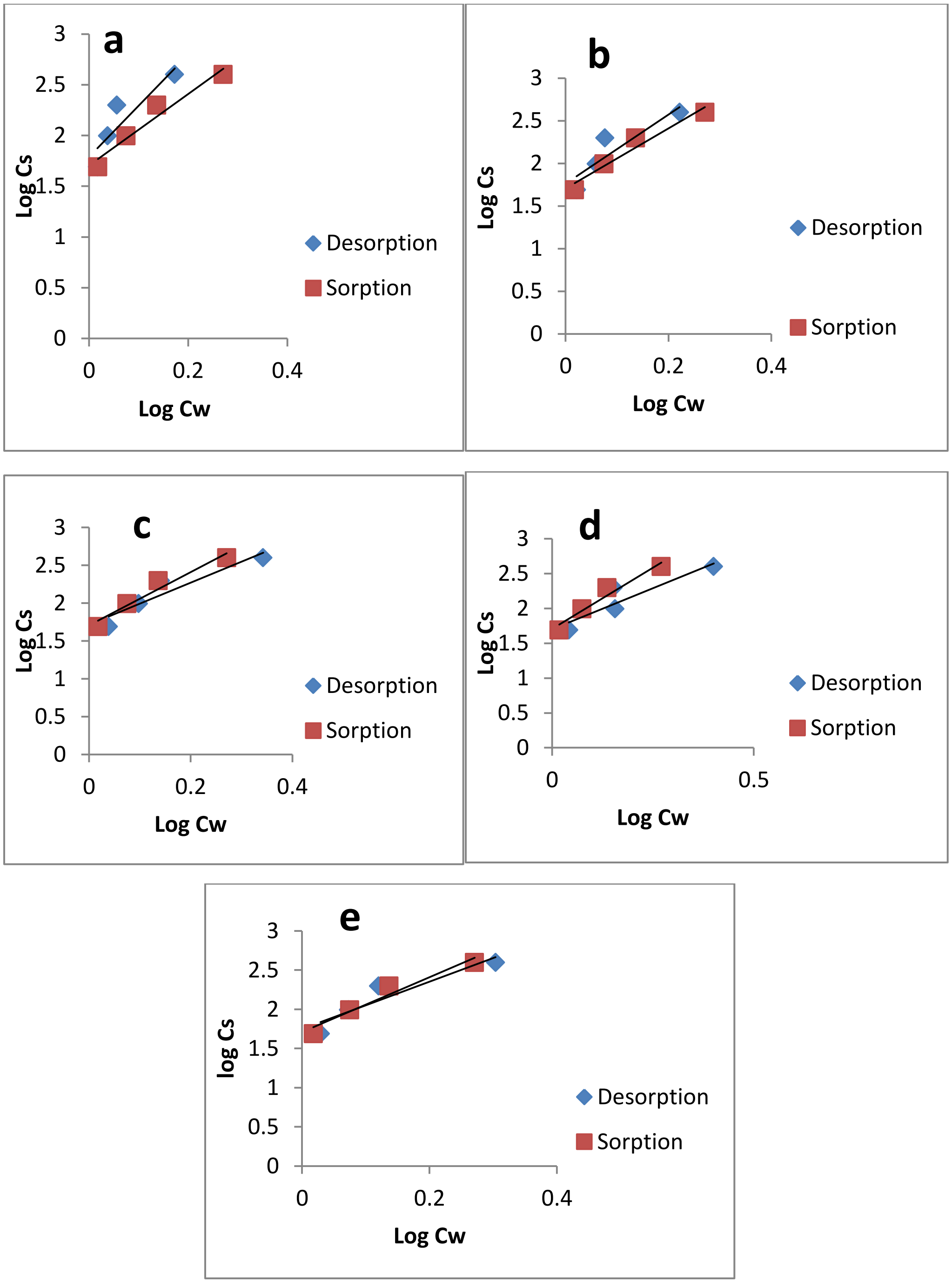

Figure 5.4 Desorption isotherms of OTC by Brij 35: a, b, c, d, e in the presence of Brij 35 at 0, 0.02, 0.5, 2.5, 5 g L^{-1}concentrations, respectively

Non-ionic surfactants are known for their ability to enhance the release of pesticides from soils. For example, Triton X-100 showed good desorption efficiency of pesticides from soil (Mata Sandoval et al., 2000). As a result of occupying sorption sites in soil, surfactant micelles compete with pesticides and this leads to their release in the solution. Furthermore, the more micelles present in the aqueous phase, the more OTC partitioning into the micelles within the solution leading to the release of higher amount of sorbed OTC. This conclusion is inconsistent with the findings of (Sun et al., 1995 and Wang and Keller, 2008). The ability of non-ionic surfactants to solubilize polar compounds is positively related to the number of ethelyne oxide groups (EO) in the surfactant molecule (Xiarchos and Doulia, 2006). The greater the number of EO groups, the more hydrophilic the surfactant (Jafverti et al., 1994). Owing to the twenty-three EO groups, Brij 35 is expected to exhibit a high ability to solubilize polar compounds.

The greater desorption of OTC versus SCP in the presence of Brij 35 could be attributed to the fact that the lower pka value could be responsible for the lower desorption potential of organic compounds (Cheftaze et al., 2004). This is in agreement with our results which demonstrate that lower amounts of SCP (pka = 5.5) are released in the solution compared to OTC (pka = 7.3). Although both SCP and OTC have an amine group in their structure, it is expected that the presence of the amine group in SCP would interact strongly with the ethoxyethylene head of Brij 35 due to the electron withdrawal effect of the Cl atom present in the SCP molecule. The ability of surfactants to release antibiotics from soils is still not clear and one study by Hari et al. (2005) indicated that sorption of acetaminophen and carbamazepine increased in the presence of the non-ionic surfactant NP9 to the extent of their hydrophobicity (K_{ow} = 0.4 and 2.45, respectively). However, nalidixic acid and norfloxacin sorption did not follow the same pattern. This indicates that sorption of a pharmaceutical is not governed by their solubility or log K_{ow}. Our findings are in agreement as it appears that OTC and SCP sorption in the presence of surfactant is not predictable in terms of their hydrophobicity.

Table 5.4 Freundlich and hysteresis coefficient TII for desorption of OTC and SCP by Brij 35 and desorption efficiency coefficient (E) after desorption with Brij 35

Brij 35 Conc. (g L^{-1})	Oxytetracycline				Sulfachloropyridazine			
	K_{Fd}	n_{Fd}	TII	E	K_{Fd}	n_{Fd}	TII	E
0 (Tap water)	61.58	5	1.42	nd	1.24	0.71	-0.47	nd
0.02	57.65	4.00	1.13	1.06	1.47	0.61	-0.25	0.94
0.25	51.28	2.77	0.78	1.15	1.76	0.58	-0.20	0.98
2.5	50.35	2.35	0.66	1.30	1.37	0.64	-0.33	0.98
5.0.	55.97	3.02	0.85	1.09	1.39	0.35	0.27	0.99

Since soil is fertilized by the addition of manure on a regular basis, several types of antibiotics are more likely to exist in the soil and consequently, the soil microbial population would be altered. Several authors investigated the effect of the presence of antibiotics on soil microbial biomass (Kotzerke et al., 2008; Thiele-Bruhn and Beck, 2005; Hammesfahr et al., 2008; Kong et al., 2006; Zielezny et al., 2006; Schmitt et al., 2005). The effect varied according to the chemical and physicochemical structure of the antibiotics; for example, tetracyclines and sulfanomides revealed a dose related inhibition on the microbial activity (Thiele-Bruhn, 2005). A recent study by Gutierrez et al. (2010) indicated that sulfanomides can negatively affect the soil microbial population at relatively low concentrations. Similarly, Heuer et al. (2011) reported that repeated manure applications increased the number of sulfanomides resistant genes (at low concentrations) in soil. Our study is a step forward to highlight the risk of applying surfactant rich water as it can lead to significant changes in the pathways of antibiotics in the soil either by increasing their bioavailability and leaching potential or by binding to soil and consequently after rainfall events, enhance their release and movement to greater depths into the soil profile.

5.4 Conclusions

The sorption and desorption hysteresis and partitioning of OTC and SCP in a water-surfactant soil system were investigated. The results reported in this study are crucial to understanding the overall fate of these compounds in the environment. Depending on the absence, or the presence, of the non-ionic surfactant Brij 35, the sorption coefficient K_F value of OTC and SCP varied accordingly. OTC sorption was high in the presence of the surfactant in the monomer form; however, it decreased dramatically once micelles were present in the solution (above CMC), indicating a solubilization effect. To the contrary, the SCP sorption coefficient increased in the presence of the surfactant in monomeric and micelles form, indicating higher affinity to sorb to the surfactant that have already sorbed to soil. Strong Hysteresis exists only in the water medium and the presence of the surfactant in the monomeric form for OTC, indicating an irreversible effect. However, no hysteresis was observed in the case of SCP. The desorption coefficient was found to decrease for OTC and SCP in the presence of surfactant. Brij 35 had the potential to release OTC from soil more than SCP. This is indicated by the higher calculated efficiency coefficient obtained for OTC compared to that for SCP. These findings indicate that the hydrophobicity for both antibiotics failed to predict their sorption behavior. Due to the fact that antimicrobial agents possess different active and ionizable groups, they can sorb to the surfactant moieties by hydrogen bonding. The extent of this process depends on the chemical properties of the surfactant and the functional groups of the antibiotics. Applying manure as a fertilizer helps to introduce these antibiotics and when combined with surfactant rich water for irrigation, it increases their leaching potential to pollute the groundwater. It also enhances the risk of developing gene resistant bacteria, which can be transferred to humans as a long term side effect.

Connecting text to Chapter 6

To meet ever increasing food demand of growing populations, high amounts of herbicides are widely used to protect crops and provide food security. As articulated in previous chapters, irrigation with surfactant- rich water can enhance the mobility of coexisting chemicals.

This chapter is based on a field experiment using the same setup in Chapters 3 and 4.

This chapter is based on a manuscript and it is currently in press in the Journal of Applied Sciences. The manuscript is co-authored by my supervisor, Dr. S. O. Prasher. The format of the original draft has been modified to remain consistent with the thesis format. All literature cited in this chapter are listed in the Bibliography (Chapter 9), at the end of this thesis.

Chapter 6 – Effect of the Presence of Nonionic Surfactant Brij 35 on the Mobility of metribuzin in soil

Eman ElSayed and Shiv Prasher

Abstract

Given the water scarcity becoming endemic to a large portion of the globe, arid region irrigation has resorted to the use of treated, partially treated, or even untreated wastewaters. Such waters contain a number of pollutants, including surfactants. Applied to agricultural lands, these surfactants could affect the fate and transport of other chemicals in the soil, particularly pesticides. A field lysimeter study was undertaken to investigate the effect of nonionic surfactant, Brij 35, on the in-soil fate and transport of a commonly used herbicide, metribuzin [4-amino-6-*tert*-butyl-3-(methylthio)-1,2,4-triazin-5(4*H*)]. Nine PVC lysimeters, 1.0 m long × 0.45 m diameter, were packed with a sandy soil to a bulk density of 1.35 mg m^{-3}. Antibiotic-free cattle manure was applied (10 mg ha^{-1}) at the surface of the lysimeters. Metribuzin was then applied to the soil surface of all lysimeters at a rate of 1.00 kg a.i. ha^{-1}. Each of three aqueous Brij 35 solutions, 0, 0.5 and 5 mg L^{-1} (*i.e.*, “good”, “poor” and “very poor” quality irrigation water) were each applied to the lysimeters in triplicate. Analysis for metribuzin residues in samples of both soil and leachate, collected over a 90-day period, showed the surfactant Brij 35 to have increased the mobility of metribuzin in soil, indicating that continued use of poor quality water could influence pesticide transport in agricultural soils, and increase the risk of groundwater contamination.

Keywords: nonionic surfactant; Brij 35; herbicide; mobility; wastewater; sandy soil

6.1. Introduction

Water is a very complex and dynamic resource and although the estimated amount of the available water on the planet is 140 billion km^3, only 3 % is fresh water (World Meteorological Organization,1997). Due to the distribution of fresh water resources around the globe, less than 1% of these resources are available for human use. This, in turn, leads to water shortage problems in many regions of the world, particularly developing countries. Water scarcity combined with poverty is forcing the reuse of untreated or partially-treated wastewater for irrigation in order to cope with the high food demands of growing populations (Rahman et al., 2012). Consequently, the risk of bacterial infections, roundworms and diarrheal diseases are much greater (Chatterjee, 2008). A recent survey revealed that the 46 countries, representing 75% of the world's irrigated land, use polluted water for irrigation (Drechel et al., 2010). Globally, an estimated 20 million ha of land are irrigated with wastewater, and this area is expected to markedly increase in the next few years (Hamilton et al., 2007).

Wastewater, originating from the discharge of municipal and industrial effluents, contains a number of inorganic and organic substances. Among organic contaminants of wastewater and sludge, surfactants are often detected at the highest concentrations (Brunner et al., 1988; Field et al., 1992; Wild et al., 1990). Non-ionic surfactants concentrations ranging from 10^2 to 10^3 mg L^{-1} have been detected in wastewater (Narkis and Ben-David, 1985). Non-ionic surfactants such as alcohol ethoxylates (AEs), alkylphenol ethoxylates (APE) are used extensively as leather degreasing agents and in other textile industry applications. Consequently, non-ionic surfactants have been identified as major contaminants in untreated wastewater from such industries (Castillo et al., 1999; Feitkenhauer and Meyer, 2002). Owing a non-dissociable hydrophilic group (e.g., alcohol, phenol, ether, ester, or amide), non-ionic surfactants do not ionize in water. Although in the wastewater treatment plants, APEs degrade into metabolites such as nonylphenol ethoxylates (NPEs), treatment plants are not adequately efficient to remove the metabolites such as environmentally damaging nonylphenols (NPs)

(Zoller, 1994; Loyo-Rosales et al., 2007). Consequently, nonylphenols (NPs) were detected at high concentrations ranging from 1.8 to 25 g L^{-1} in two rivers in Switzerland (Bhandari et al., 2009). Further, studies showed that the continuous use of household products containing AEs, contributes to NPE and NP loads in urban sewer waters (Conn et al., 2006; Loyo-Rosales et al., 2007).

Certain AEs are now used as an alternative to alkyl polyphenol ethoxylates (APEOs), as they are safer as result of their rapid breakdown to less toxic, less persistent and less estrogenic compounds. Generally, the presence of nonionic surfactants in irrigation water leads to two major concerns: (1) The degradation products of non-ionic surfactants such as nonylohenol ethoxylates (NPEO) and NP act as estrogen mimicking compounds, leading to symptoms like change in sex ratio, decrease in fish population and malformations in some aquatic animals (Esperanza et al., 2004). In terms of the estrogenic effects, a study in US raised a great concern of potable water contamination by NPs which have been detected in some wells. The authors reported that the source of these compounds is the continuous infiltration disposal of wastewater treatment plant effluents (Barber et al. 2009). (2) Non-ionic surfactants in the irrigation water may have an impact on the mobility of chemicals in soil and cause contamination of groundwater (Huggenberger et al., 1973; Kan and Tomson, 1990; Aronstein et al., 1991; Rodriguez-Cruz et al., 2004). Katagi (2008) reported that the downward movement of pesticides in soil was enhanced by the presence of high non-ionic surfactant concentrations in leaching water. However, the effect may depend on the surfactant concentration. Similarly, Tao et al. (2006) indicated that, at low concentrations 0–20 mg L^{-1}, surfactants have the potential to decrease sorption and thus mobilize herbicides such as atrazine. For example, at low concentrations (0.04 g kg^{-1}), non-ionic surfactants decreased the mobility of the herbicide metolachlor in soil; however, at high concentrations (5–50 g kg^{-1}), the mobility increased (Sanchez-Camazano et al., 1995). A lysimeter study revealed that at a low concentration (12 mg L^{-1}), NP had no effect on the mobility of atrazine, metolachlor and metribuzin in sandy soil (Nilufer, 2005).

Pesticide contamination of water bodies has generated a great deal of concern. Generally, it results from diffuse (non-point) sources such as runoff and leaching from agricultural lands. Triazinones herbicides, such as metribuzin (4-amino-6-*tert*-butyl-4,5-dihydro-3-methyltio-1,2,4-triazin-5-one), are used worldwide to control broadleaf weeds in crops such as potatoes (*Solanum tuberosum* L.), soybeans [*Glycine max* (L.) Merr.] and other vegetable crops. Highly water soluble (1050 mg L^{-1}) and having a low adsorption coefficient (K_{oc} = 60), metribuzin shows moderate persistence in soil. Consequently, it may have the potential to leach into the soil profile and thus contaminate groundwater. Further, metribuzin was detected at the highest concentration of 25 μg L^{-1} in Lake Erie tributaries (Richards et al., 1993) and found to be the most frequently detected herbicide with a maximum concentration of 0.351 μg L^{-1} in 20 samples from drinking water wells in Brazil (Dores et al., 2006). The half-life of metribuzin in soils ranges from 11 to 46 days in lab and field experiments; however, it was reported to be as long as 60–90 days under winter conditions in Manitoba (Webster, 1979). In terms of the toxicity to aquatic plants, Fairchild et al. (1998) stated that compared to atrazine, metolachlor and alachlor, metribuzin exhibits the highest level of toxicity. Similarly, metribuzin is highly toxic to freshwater macrophytes and algae under laboratory conditions (at EC_{50} = 31 μg L^{-1}) (Fairchild et al., 2002). Recently, Plhalova et al. (2012) investigated the effect of metribuzin in surface water on fish and found that the lowest observed effect concentration (LOEC) is 33 mg L^{-1}.

Studies have shown that metribuzin dissipation is primarily dependent upon degradation by soil microorganisms (Ladlie et al., 1976; Sharom and Stephenson, 1976; Khoury, 2001). Non-ionic surfactants are commonly used in herbicide formulations to enhance the herbicide penetration through the plant cuticle and thus increase its efficiency by reducing the loss of applied herbicide (Ramsey et al., 2005). Since irrigation with wastewater can introduce large amounts of surfactants to soil, this could enhance the mobility of pesticides, such as metribuzin in soil water systems, by increasing their water solubility. To the best of the authors' knowledge, no study has investigated the fate and transport of metribuzin in the presence of rich surfactant irrigation water under field conditions and the potential contamination of ground water. Therefore, the aim of this study was to investigate the effect of the presence of the non-ionic surfactant Brij 35 in irrigation wastewater at concentration above CMC on the downward movement of metribuzin in the soil profile and leachate.

6.2. Materials and Methods

6.2.1. Chemicals and reagents

A pure standard (Pestanal®) and formulation (Sencor 75) of metribuzin; trifluralin, used as an internal standard; the non-ionic surfactant Brij 35 [Polyoxyethylene lauryl ether $(C_2H_4O)_{23}$-$C_{12}H_{25}OH$] with critical micelles concentration (CMC) = 74 mg L^{-1} ; and HPLC-grade methanol and acetonitrile were obtained from Sigma-Aldrich. Mobile phase chemicals were purchased from Fisher Scientific. Double–deionized water (Milli-Q, Millipore, Molsheim, France) was used in the preparation of standard solutions and mobile phase solutions.

6.2.2. Soil characteristics

Belonging to the St. Amable complex, the sandy soil used was obtained from a field in the Macdonald Campus of McGill University, Ste-Anne-De-Bellevue, Quebec. Physical and chemical properties of soil are given in Table 1.

Table 6.1-Physical and Chemical Characteristics of Soil

Soil Type	Sand (%)	Silt (%)	pH	Bulk Density (Mg m^{-3})	Organic Matter (%)	CEC (cmol kg^{-1})	Hydraulic Conductivity (cm d^{-1})	Zero point of charge (zpc)
Sand	92.2	4.3	5.5	1.350	2.97	4.9	1.67 (*S.D. = 0.45)	3.4

*S.D. stands for standard deviation

6.2.3. Sorption study

Sorption of metribuzin onto soil in the presence of the non-ionic surfactant Brij 35 was investigated through a soil equilibrium technique. Triplicate soil samples (1g) were equilibrated with an aqueous solution (10 mL) of metribuzin at concentrations of (2.5, 5.0, 7.5 and 12.5 µg mL^{-1}) in factorial combination with Brij 35 concentrations of 0, 0.5 and 5 g L^{-1}. All solutions contained 0.01 M $CaCl_2$ to mimic the ionic strength of groundwater (Wilde et al., 2008). The soil slurry was placed in a 50 mL centrifuge tube, and placed on a reciprocal shaker, operating at 200 rpm, for 24 hrs. The slurry was centrifuged at 2683 g for 20 min. Extraction and analysis of metribuzin proceeded, as described above. The proportion of metribuzin adsorbed was calculated by taking the difference between the amount initially present in solution and the amount remaining in solution, after equilibrium with the soil.

The sorption coefficient was calculated as follows:

$$K_d = \frac{C_s}{C_{aq}} \qquad \text{Eq. 6.1}$$

Where

C_s is the amount of metribuzin sorbed (µg g^{-1});

C_{aq} is the solution concentration in µg mL^{-1}; and

K_d is the sorption coefficient (mL g^{-1})

Organic carbon normalized coefficient values for metribuzin in the absence of surfactant and in the presence of surfactant were obtained as follows:

$$K_{oc} = \frac{K_d}{f_{oc}} \qquad \text{Eq. 6.2}$$

Where

f_{oc} is the organic carbon fraction of the soil (0.0297 g g^{-1} for the soil used); and K_{oc} is the partition coefficient of the contaminant in the organic fraction of the soil (mL g^{-1}).

6.2.4. Experimental set up

The field experiment investigating metribuzin transport in a sandy agricultural soil was conducted in nine outdoor PVC lysimeters set up at the Macdonald Campus of McGill University, Ste-Anne-De-Bellevue, Quebec. The lysimeters were irrigated with three different levels of surfactants and applied in each lysimeter using the completely random design. The lysimeters were (0.45 m O.D. × 1 m long), sealed at the bottom to 0.6 m × 0.6 m PVC sheets. Each was packed in layers with a sandy soil and adjusted to a bulk density of 1.35 Mg m^{-3}. A 0.05 m diameter drainage pipe was installed at the bottom of each lysimeter. Four, 10 mm diameter, soil sampling holes were made in each lysimeter at depths of 0.1, 0.3 and 0.6 m the soil surface (Fig 6.1). The lysimeters were sheltered to prevent entry of natural precipitation.

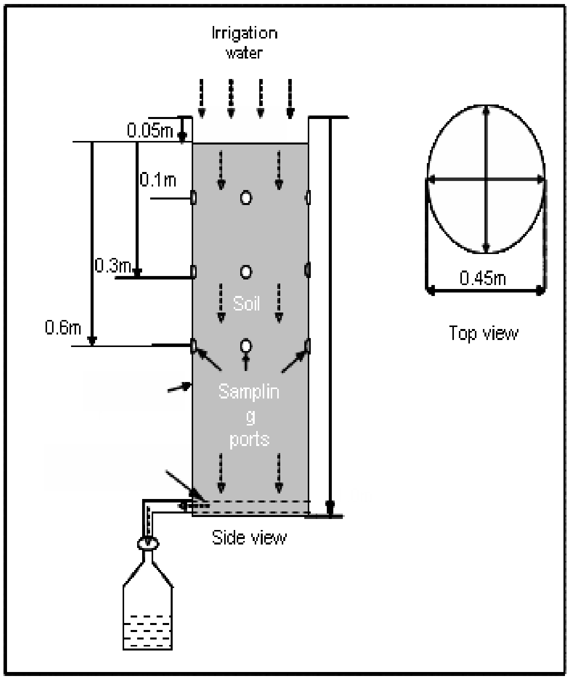

Figure 6.1 Schematic design of the lysimeter

6.2.4.1. Application of tested compounds

Cattle manure was collected from an organic farm in Ham-Sud, Québec, at the end of June 2009. Before the start of the experiment, all lysimeters were irrigated, bringing them to saturation. The drainage pipe at the bottom of each lysimeter was left open throughout the study. The next day (Day 0), with the lysimeter's soil at field capacity**,** homogenized manure (10 Mg ha^{-1}) was applied to the surface of all lysimeters and manually mixed into the top 30 mm of soil (Chettri and Thapa, 2004). Metribuzin was then sprayed on to each lysimeter's soil surface (July 1, 2009) at the locally recommended rate for potatoes (1 kg a.i. ha^{-1}). Twelve liters (70 mm) of irrigation water, containing one of three different concentrations of Brij 35 (0, 0.5 or 5.0 g L^{-1}) was applied on day 0, day 21, day 42, day 63, according to recommended irrigation practices for potatoes. Each treatment was replicated three times. While these surfactant concentrations may appear to be high, they are well within concentrations found in wastewater and industrial wastewater. Indeed, concentrations of up to 10 g L^{-1} have been used to study the effect of surfactants on atrazine movement in soils (Abu-Zreig et al., 1999).

6.2.4.2. Soil and leachate sampling

Soil samples were collected at the surface as well as 0.1, 0.3 and 0.6 m beneath it, through 4 sampling ports in the side of the lysimeters. Soil samples were collected on 8 occasions: 0, 1, 5, 11, 22, 43, 60 and 90 days after the application of manure. For each surfactant concentration, three replicate soil samples (3 lysimeters) were taken at each of the four depths, and samples from a common treatment × depth were combined in a composite sample (~15 g). Subsamples of about 5 g were taken from each composite sample, and their moisture content was determined. The remaining portions of the samples were stored in sealed bags in the freezer at -4ºC until extraction. Leachate samples (1 L) were collected as a subsample of a total of approximately 9-11 L of leachate, collected at the outlet at the bottom of each lysimeter, following each of the four irrigation events. The subsamples were then transported to the lab and immediately extracted to prevent any chance of metribuzin degradation.

6.2.5. Mass balance calculations

At each sampling date, total herbicide mass, recovered from each lysimeter, was calculated as the sum of herbicide recovered in soil samples across all depths of the soil profile. Adding the herbicide mass in the leachate to that in the soil would total the initial herbicide mass applied, minus any losses (unrecovered metribuzin) due to degradation or volatilization (Eq. 6.3) (ElSayed et al., 2013).

$$MTR_{init} = 1590.4\,\rho\,\left[C_{(0-5)}\theta_{(0-5)}\,h_{(0-5)} + C_{(5-15)}\theta_{(5-15)}h_{(5-15)} + C_{(15-45)}\theta_{(15-45)}h_{(15-45)} + C_{(45-70)}\theta_{(45-70)}h_{(45-70)}\right] + \left[C_{leach}V_{leach}\right] + MTR_{lost} \qquad \text{Eq. 6.3}$$

Where

MTR_{init}	Total metribuzin (mg) initially applied
MTR_{lost}	Metribuzin lost through degradation, volatilization, etc. (mg)
ρ	Soil bulk density, (g cm^{-3})
$C_{(x-y)}\theta_{(x-y)}h_{(x-y)}$	Metribuzin concentration and soil moisture content, respectively, in soil layer *h* ranging from depth x to depth *y* (mg g^{-1})
C_{leach}	Metribuzin concentration in leachate (mg L^{-1})
V_{leach}	Volume of leachate
1590.4	Soil layer surface area, $\pi\left(\frac{D}{2}\right)^2$, where D = 45 cm

In order to calculate the mass of metribuzin recovered in the soil layer samples, the following equation was used for this purpose

$$\text{Mass of MTR} = [C\ (m)] * \rho * a * h \qquad \text{Eq. 6.4}$$

Where

C is the laboratory reported analytical metribuzin concentration in soil samples (mg g^{-1});
m is the moisture content of soil samples (mass water /mass dry soil mg g^{-1});
ρ is soil bulk density (g cm^{-3});
a is the cross-sectional area of the lysimeter (m^2); and
h is the sampling depth of soil layers (cm).

The half-life $t_{½}$ of metribuzin was calculated as follows

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} \qquad \text{Eq. 6.5}$$

Then equation 6.6 is used in order to calculate k

$$C = C_0\, e^{-kt} \qquad \text{Eq. 6.6}$$

Where
C is the metribuzin concentration at time (t);
C_0 is the initial concentration of metribuzin; and
k is the degradation rate constant.

6.2.6. Analytical methods

6.2.6.1. Leachate sample extraction

Each 1 L subsample was filtered through 90 mm filter paper, followed by filtration through a 45 mm filter (Advantec Dublin, CA, USA), to remove coarse and fine suspended matter, prior to extraction. Metribuzin-binding MCX cartridges (Oasis Co., Ltd., NY, USA) were used in solid phase extraction (SPE). Prior to this extraction, trifluralin was added to each of the filtered samples as an internal standard. Preconditioning of each cartridge began by passing 5 mL of water through each cartridge twice, then 5 mL of 50:50 water: methanol (*v*/*v*), followed by 100% methanol, all at a flow rate of 10 mL min^{-1}. The sample filtrate was then passed through the cartridges then washed twice with 5 mL of water, to elute the metribuzin and trifluralin. Collected in a test tube, the 10 mL of eluate was evaporated under a N_2 stream, residue redissolved in 1 mL of acetonitrile, then passed through 0.22 µm syringe driven filter (Millex-GV, Billerica, MA, USA) and filtered solution transferred to a vial for HPLC analysis.

6.2.6.2. Soil sample extraction

In a 50 mL centrifuge tube, to each soil sample (10 g on fresh weight basis), 20 mL of ACS methanol was added, along with trifluralin as an internal standard, and the slurry was vortexed for 30 s. The tube was then placed in an ultrasonic bath for 15 min, and then centrifuged at 2683 g for 20 min. The supernatant was decanted and the extraction procedure was repeated twice more. The combined supernatants were passed through a 45 mm filter paper, and then evaporated under a N_2 stream. Samples were redissolved in 1 mL of acetonitrile and passed through 0.22 µm syringe driven filter prior to HPLC analysis.

6.2.6.3. Analysis

The soil samples and leachate were analyzed by HPLC, equipped with diode array detection (DAD) and an Eclipse plus C_{18} column (4.6 × 150 mm; Agilent, USA). The mobile phase was acetonitrile and water, run as a gradient; 50:50 acetonitrile: water (v/v) for 9 min then change to 10:90 acetonitrile: water (v/v) for 8 min. The flow rate was 1 mL min^{-1} and the detection wavelengths were 238 nm and 254 nm for metribuzin and trifluralin, respectively. The extraction efficiency found to be 93% (representing 3 replicates from each concentration) and the detection limit of this method for the tested compound (metribuzin) was 10 ng g^{-1}.

6.2.7. Data Analysis

A statistical model using repeated measures over time and depth was employed to determine if the metribuzin concentrations differed between treatments, over time and over depth. Data was analysed with PROC MIXED in SAS v. 9.2 (SAS Institute Inc., 2010).

6.3. Results and Discussion

6.3.1. Sorption

Among many factors affecting the transport of chemicals in soil, sorption plays an important role; therefore, sorption experiments in the presence and absence of Brij 35 were carried out. Results revealed that the amount of metribuzin sorbed was higher in the absence of Brij 35; however, it decreased in the presence of Brij35 at concentrations above CMC. The sorption isotherms of metribuzin in tap water and Brij 35 solutions at concentrations of 0.5 and 5 g L^{-1} (Fig. 6.2) all showed a good fit ($R^2 \geq 0.97$) with Equation (6.1). The K_d value for metribuzin shows the highest 1.80 mL g^{-1} in the absence of the surfactant; however, it decreases significantly to (0.93 and 1.38) in the presence of Brij 35 at 0.5 and 5 g L^{-1}, respectively (Table 6.2). This indicates that the presence of micelles may enhance the release of sorbed metribuzin into the solution. Furthermore, a study by Sun et al. (1995) revealed that non-ionic surfactants at concentration above CMC decreased the sorption coefficient K_d of hydrophobic organic compounds (HOCs). Similarly, Chappell et al. (2005) indicated that Brij 35 at concentration above CMC competes with atrazine for sorption sites in soil leading to a significant decrease in atrazine sorption. Furthermore, the presence of surfactants enhanced the solubility of Trichloroethylene (TEC) and therefore, higher desorption rate of TEC in the aqueous medium has been observed (Zhang et al., 2011).

As a result of increasing the concentration of Brij 35 from 0.5 to 5 g L^{-1}, K_d values increased from 0.93 to 1.38. This slight increase could be explained by the fact that at higher concentrations, non-ionic surfactant sorbed strongly to the soil and formed bilayers and metribuzin has an affinity to partition with the hydrophilic head of Brij 35, presumably via hydrogen bonding. This may lead to enhance metribuzin partitioning into the surfactant which is already sorbed to soil (Liu et al., 1992; Mata-Sandoval et al., 2000) Therefore, increasing the K_d values at the highest Brij 35 concentration of 5 g L^{-1} was observed. Furthermore, Nilufar (2005) stated that the sorption coefficient of metribuzin (K_d) was 41% lower in the presence of the nonionic surfactant degradation product nonylephenol (NP) below CMC, confirming the desorption potential of NP for metribuzin.

The aqueous concentration of metribuzin increased once CMC is exceeded. This enhances micelles to form in the solution and compete with the sorbed surfactant for metribuzin. The more micelles present in the aqueous phase, the more metribuzin partitioning into the micelles within the solution, resulting in greater amount released from sorbed metribuzin. The present results are in agreement with the findings of Sun et al. (1995) and Wang and Keller, 2008). Also, our results are in good match with Genari et al. (2009) who indicated that the interaction between the surfactant and soil led to a competition with pesticides for adsorption sites, therefore a decline in pesticides adsorption was observed.

The distribution coefficient K_{oc}, normalized to the corresponding soil organic carbon fraction f_{oc} and calculated from Equation (6.2), is found to follow the same trend as K_d values.

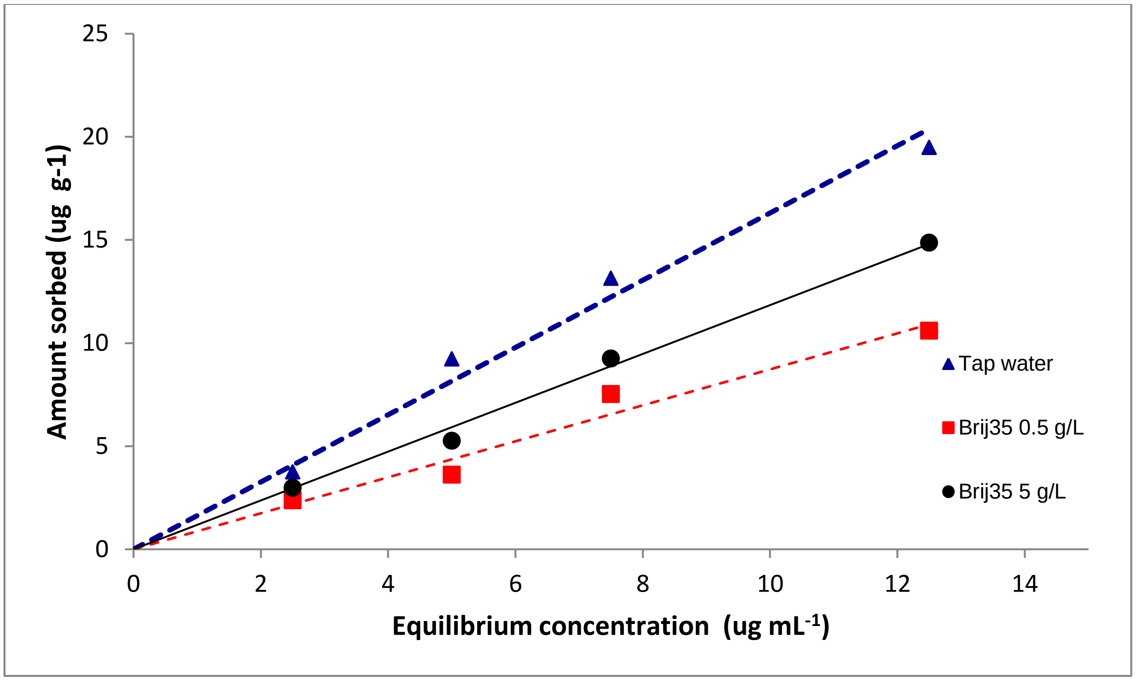

Figure 6.2 Metribuzin isotherms in the absence and presence of the non-ionic surfactant Brij 35

Fundamentally, K_{oc} values have been used as an indicator of the leaching potential of herbicides such as atrazine and metribuzin (Southwick et al., 1995). In fact the K_{oc} value of 60.61 for metribuzin in the absence of Brij 35 has been documented in the literature (Comfort et al., 1994; Weber 1994; Bedmar et al., 2004). Obviously, the calculated K_{oc} values show a higher leaching potential for metribuzin in the presence of Brij 35 (31.31 – 45.46) compared to the value of 60.61 in the absence of Brij 35. This highlights the potential of non-ionic surfactants to enhance the desorption of metribuzin, either by solubilization or partitioning into the surfactant's micellar core.

6.3.2. Mass balance

The mass balance for metribuzin is presented in (Table 6.3). For all irrigation treatments, metribuzin concentrations were found to be below the detection limit by day 90.

Table 6.2 Distribution coefficient K_d, R^2 and K_{oc} values for metribuzin sorption in the presence of the nonionic surfactant Brij 35

Concentration of Brij 35 (g L^{-1})	K_d	R^2	K_{oc}
0	1.8	0.97	60.61
0.5	0.93	0.95	31.31
5	1.38	0.99	46.46

In both the water and surfactant-irrigated treatments, the total amount of metribuzin detectable in the system (soil + leachate), declined from an initial (applied) level of about 20 mg to less than 3 mg after 63 days and four irrigations. The relative amount of metribuzin in the two lower soil depth layers (15–45 cm and 45–70 cm) to that in the upper layers (0–5 cm and 5–15 cm) was at least 2-fold greater in the presence of surfactants from Day 5 onwards; suggesting that a greater quantity of metribuzin leached downwards in the presence (*vs.* absence) of the surfactant. This will be further addressed in the discussion of metribuzin residue concentrations in the soil which follows.

From 15 days onward, the total amount of measured metribuzin was higher in the treatments of surfactant compared to the tap water (Table 6.3). After 60 days, the total residual metribuzin was 4 and 6 fold greater in the 5 and 0.5 g L^{-1} treatments, respectively, than in the tap water treatment. The percentage of unrecovered metribuzin (Fig. 6.3) was similar for all three irrigation types up to 5 days; however, later values were smaller in the presence of surfactant. As a result, greater recoveries have been measured in the presence of the non-ionic surfactant Brij 35 compared to tap water treatment. Despite the fact that metribuzin is mobile in soil, previous studies detected no amount of metribuzin in leachate from lysimeters packed with sandy soil and irrigated with tap water (Nulifar, 2006; Fan, 2010). However, in the present study, 0.34% of the applied metribuzin was recovered in the leachate of lysimeters irrigated with tap water, and 1.86 and 2.04%, respectively, for the 0.5 and 5.0 g L^{-1} surfactant treatments.

Degradation of pesticides has been extensively studied and revealed the fact that some factors other than leaching, can significantly affect the breakdown of metribuzin in soil and water. These factors could be sorption, microbial degradation and photolysis (Pandiselvi et al., 2012). In general, several studies have indicated that the microbial activity plays a major role in the degradation process of metribuzin in soil (Sabadie, 1997; Jurado-Exposito et al., 1995). More specifically, soil microorganisms have the ability to transform metribuzin to its metabolites; desaminometribuzin (DA), desaminodiketometribuzin (DADK), and diketometribuzin (DK) (Kjaer et al., 2005). In sewage effluents, In the case of non-ionic surfactants, they are subject to biodegradation and produce intermediates which are generally less water soluble such as polyethylene glycols

(PEG) and carboxylic aerobic metabolites i.e., carboxylated PEGs (Soares et al., 2008).

In terms of the amount of unrecovered metribuzin in soil, results showed that in the presence of surfactant, the amount of unrecovered metribuzin was less than the one in the tap water treatment indicating that the non-ionic surfactant could have influenced metribuzin degradation in soil. As indicated in (Fig. 6.3) the presence of surfactant reduced the loss of metribuzin. This may be explained by the findings of Laha and Luthy (1992) that showed a decrease in phenanthrene degradation in the presence of non-ionic surfactants above CMC compared to those below CMC. They assumed that micelles can hold the pesticide from transporting to bacterial cells resulting in an inhibition of bactaerial mineralization of the pesticide. Similarly, comparing to Brij 30 and Triton X-100, Brij 35 reduced the bioavailability of phenanthrene as a result of the deficient interaction between the hydrophilic moiety of Brij 35 (long polyethoxy chain) and bacterial cell membrane (Guha and Jaffe, 1996). This assumption has been confirmed by Allen et al. (1999) who found that cell disruption of microbes is the main cause of inhibition of PAHs degradation, in the presence of nonionic surfactant, Triton X-100.

6.3.3. Effect of nonionic surfactant Brij 35 on metribuzin residues in soil

The repeated measures analysis showed the effect of treatment (surfactant concentration), depth and time, as well as their single and multiple interactions were all significant ($p \leq 0.05$). Mean metribuzin concentrations in soil over a 90-day period for the soil surface and at 0.1, 0.3 and 0.6 m soil depths are illustrated in Figures 6.4, 6.5, 6.6, 6.7. As expected, the metribuzin concentration was highest at the soil surface and dropped significantly as sampling depth increased. At the soil surface, the concentration decreased as the degradation rate increased with time.

Table 6.3 Metribuzin mass balance. Amounts of metribuzin (mg) in different soil profile depth rages, cumulated in leachate, and overall, over a 63 day period. Soil samplings on days 0, 1, 15, 22, 30, and 60 at depths of 2, 10, 30 and 60 cm depths, as well as and irrigations followed by leachate sampling on Days 1, 21, 42, 63. (— implies metribuzin was below the detection level)

Day	Irrigation solution Soil profile depth range (cm)/Cummulative Leachate/Total																	
	Tap water						Brij 35 @ 0.5 g L^{-1}						Brij 35 @ 5 g L^{-1}					
	0-5	5-15	15-45	45-70	Leach cumul	Total	0-5	5-15	15-45	45-70	Leach cumul	Total	0-5	5-15	15-45	45-70	Leach cumul	Total
0	19.25	— Irrigation I —			0.0	19.25	19.85	— Irrigation I —			0.0	19.85	20.06	— Irrigation I —			0.0	20.06
1	9.62	8.90	—	—	0.09	18.61	10.30	2.13	5.72	—	0.34	18.49	8.49	2.75	6.65	—	0.65	18.54
5	5.05	3.08	0.94	—	0.09	9.16	4.91	1.79	2.55	—	0.34	9.59	2.82	2.26	3.52	—	0.65	9.25
15	2.59	1.05	1.95	—	0.09	5.68	1.88	0.11	4.93	1.99	0.34	9.25	1.54	0.33	2.44	3.29	0.65	8.25
21	—— Irrigation II ——				0.17	5.76	—— Irrigation II ——				0.80	9.71	—— Irrigation II ——				1.27	8.87
22	1.32	0.21	1.36	—	0.17	3.06	0.78	—	1.60	1.72	0.80	4.90	0.95	—	0.91	1.09	1.27	4.22
30	0.85	—	—	—	0.17	1.02	0.62	—	0.82	0.56	0.80	2.80	0.22	—	1.20	1.08	1.27	3.77
42	—— Irrigation III ——				0.25	1.10	—— Irrigation III ——				1.33	3.33	—— Irrigation III ——				1.55	4.05
60	0.12	—	—	—	0.25	0.37	0.09	—	—	0.93	1.33	2.35	0.07	—	—	0.17	1.55	1.79
63	—— Irrigation IV ——				0.25	0.37	—— Irrigation IV ——				1.54	2.56	—— Irrigation IV ——				1.55	1.79

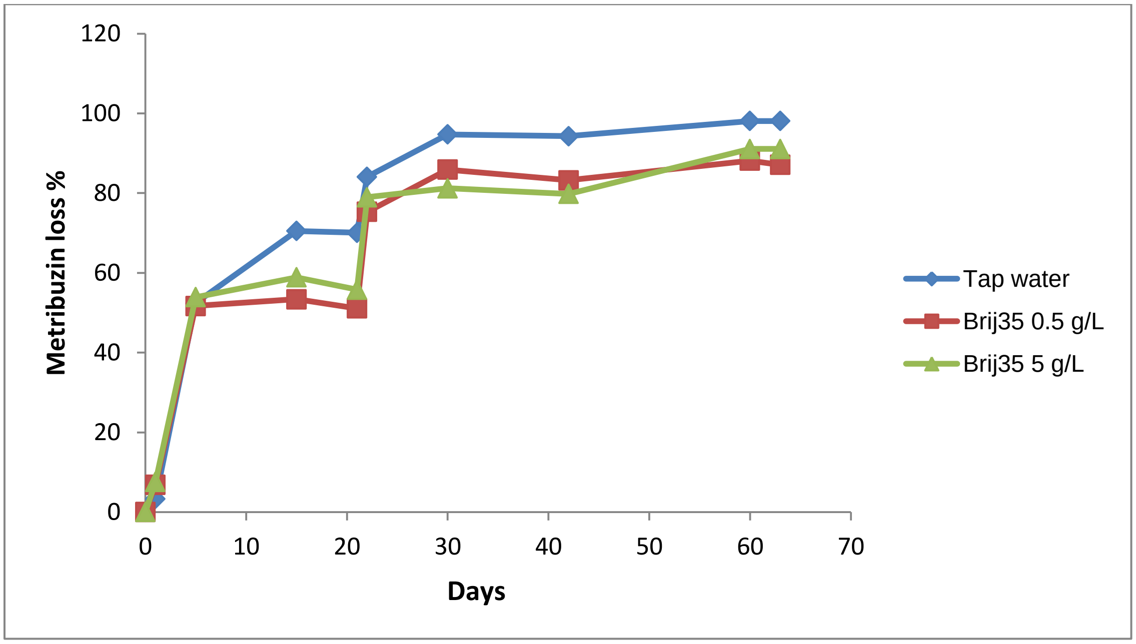

Figure 6.3 Metribuzin lost percentage in the season in the absence and presence of surfactant

The concentrations right after the first application on day 1 were 968.68, 1036.34 and 854.93 µg kg^{-1} in the treatments with tap water, Brij 35 0.5 g L^{-1} and Brij 35 5 g L^{-1}, respectively. Metribuzin levels declined over time and reached 12.37 µg kg^{-1} in the topsoil on day 60 for the tap water treatment, whereas for Brij 35 0.5 g L^{-1} and Brij 35 5 g L^{-1}, concentrations were lower at 9.82 and 7.29 µg kg^{-1}, respectively. By day 90, metribuzin concentration in the topsoil was below the detection limit for all irrigation treatments. However, a considerable amount of metribuzin leached to the next depths in the treatments with surfactants. This result for the tap water treatment concurs with the findings of several studies (Savage 1977; Bouchard et al., 1982; Fuscaldo et al., 1999; Selim, 2003; Henrikson et al., 2004). They reported that metribuzin concentrations declined in topsoil immediately after application. A number of studies suggest that a significant portion of this decline can be attributed to the presence of soil microorganisms, which play a significant role in the breakdown of metribuzin in soil (Villaverde et al., 2008; Maqueda et al., 2009).

For all treatments, metribuzin degradation is shown to follow the first order kinetic (Bowman, 1991; Di et al., 1998). Typically, a rapid initial dissipation is followed by a gradual decline in the degradation rate and eventually a relatively slow long term breakdown. The half-life of metribuzin under the experiment conditions is calculated. In the tap water treatment, the half-life of metribuzin was 8.89 days; however, it decreased to 8.35 and 7.96 days in the treatment with surfactant at 0.5 and 5.0 g L^{-1}, respectively. This is consistent with the reported half -life by Webster and Reimer (1979).

At the 0.1 m depth, initial metribuzin concentrations in the tap water treatment were higher than those in either of the Brij 35 treatments. For all treatments, metribuzin levels decreased over time; however, in the tap water treatment, metribuzin was detectable through day 22, whereas in the Brij 35 treatments it only remained detectable through day 15. This disappearance of metribuzin could be attributed to its movement to lower depths and to the microbial degradation. Metribuzin breakdown varies according to soil layers (Di et al. 1998) due to the differences in their microbial populations. Indeed, Bouchard et al. (1982) and Danial et al. (2002) observed that metribuzin degradation is decreased by depth. Likewise, Fan (2010) conducted a lysimeter study and observed that a considerable amount of surface-applied metribuzin had migrated through a sandy soil to a depth greater than 0.1 m within the first 7 days, and then decreased gradually afterwards. Similarly, results from a study investigating the mobility of metribuzin under free drainage conditions, revealed that a significant portion of surface-applied metribuzin was detected below a 0.1 m soil depth, six days after application (Jebellie and Prasher, 1998).

At the 0.3 m depth, the effect of surfactant treatments contrasted with the 0.1 m depth, since metribuzin concentrations were higher in the presence of surfactant compared to the tap water (Fig. 6.6). This indicates that Brij 35 influenced the downward movement of metribuzin. Given that metribuzin is a non-ionic compound, belonging to the weakly basic triazines, its sorption to soil is dependent on the amount of organic matter, clay content and pH. It was reported that metribuzin showed a great potential for leaching in soil (Bedmar et al., 2004; Daniel et al., 2002). At the 0.6 m depth, low concentrations of metribuzin (33.46–2.87 μg kg^{-1}) were detected from day 15 to day 60, in the Brij 35 treatments, but remained below detection limits for the tap water treatment. This highlights the role of surfactants in enhancing metribuzin mobility in the soil profile (Fig. 6.7).

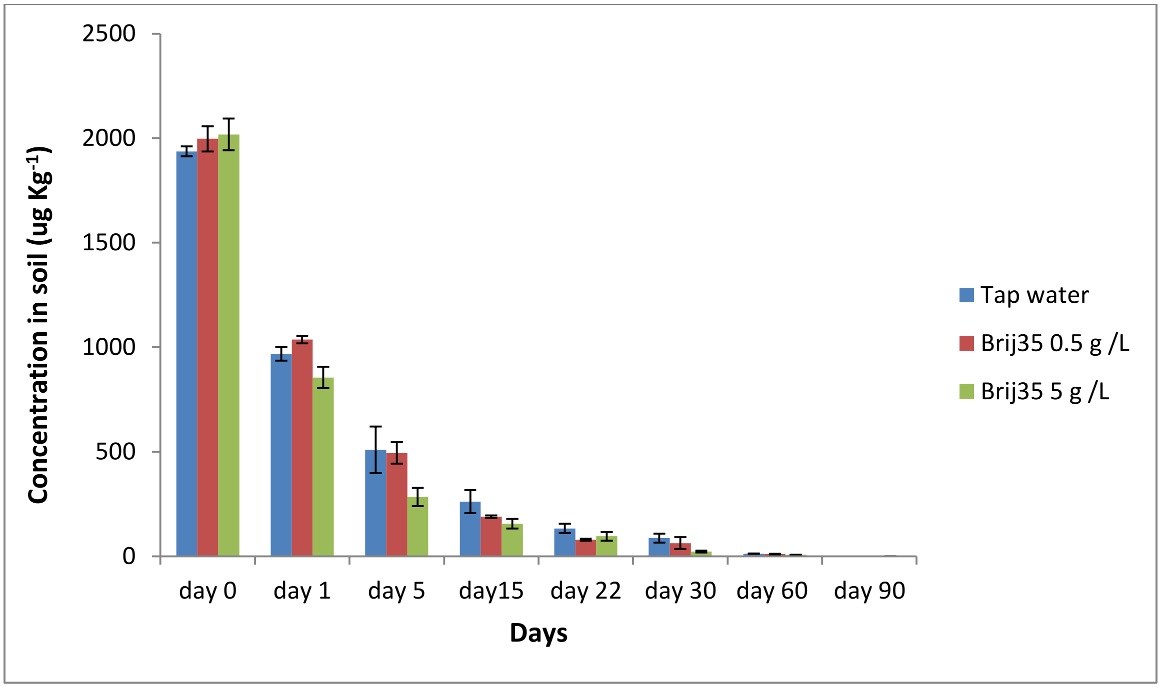

Figure 6.4 Metribuzin concentration in the soil at the surface

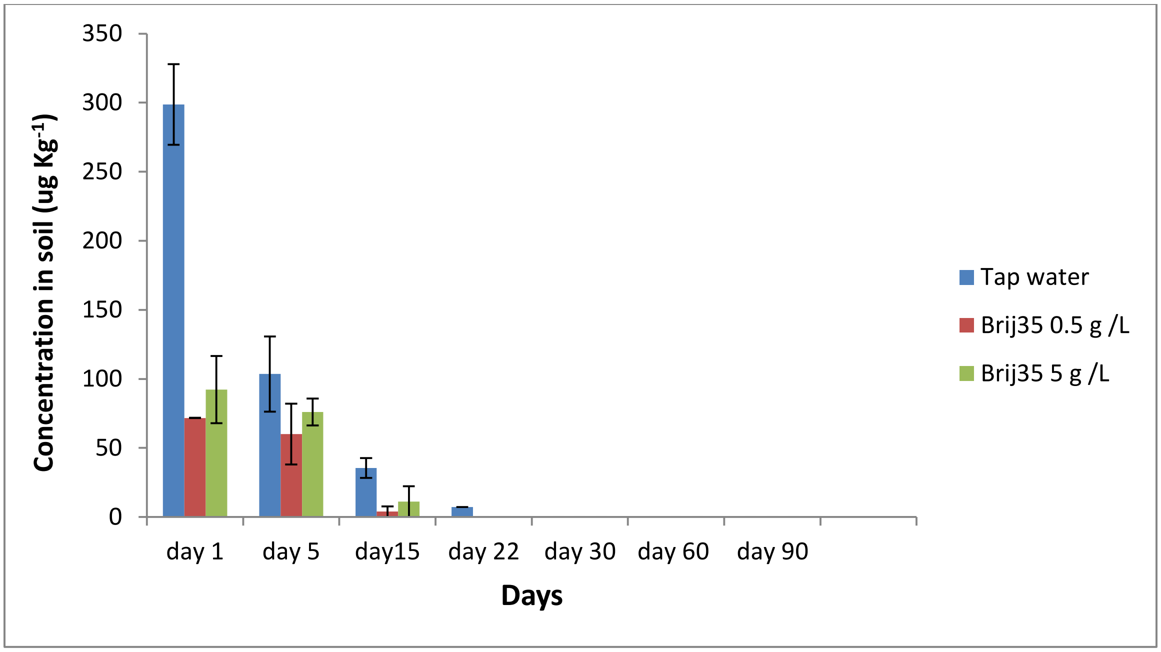

Figure 6.5 Metribuzin concentration in the soil at 0.1 m depth

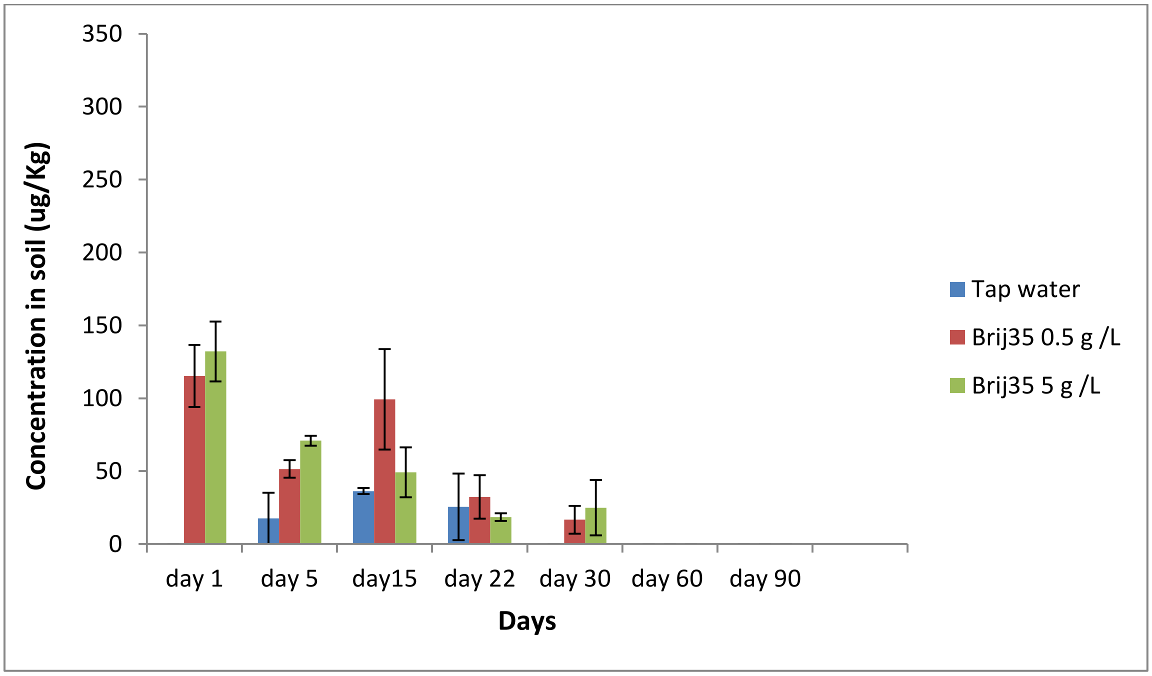

Figure 6.6 Metribuzin concentration in the soil at 0.3 m depth

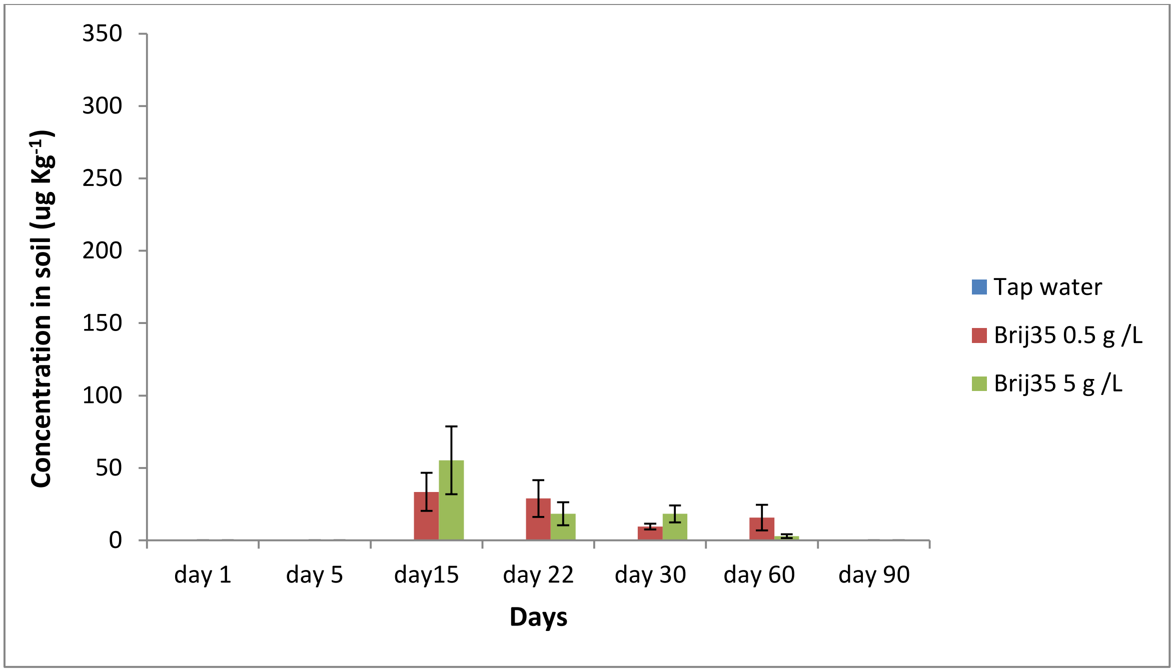

Figure 6.7 Metribuzin concentration in the soil at 0.6 m depth

The decrease in metribuzin concentrations over time and depth was reflected by the significant effects ($p \leq 0.05$) of treatment, depth, time and their interactions. Results for tap water concurred with the results of columns studies conducted by Bedmar et al. (2004) and Maqueda et al. (2009). They indicated the absence of metribuzin in soil samples from soil depths exceeding 0.30 m. Moreover, as the solubility of the herbicide increased, its ability to compete with organic surfaces decreased. This accounts for why, in certain conditions, the migration of metribuzin downward through the soil profile was improved (Olness et al., 2002).

Generally, surfactants play an important role in enhancing the mobility of pesticides and this fact has been confirmed by Muller et al. (2007) and Zhang et al. (2011). Our study also showed a greater downward movement of metribuzin through a sandy soil in the presence (*vs.* absence) of the non-ionic surfactant Brij 35. Generally, surfactants can increase the solubility of pesticides through their solubilization in the micelles, which formed above the critical micelle concentration (CMC) of the surfactant. Depending on this concentration, pesticide properties, the degree and the location of solubilization into the micelle, surfactant effects can vary. Since metribuzin is a polar herbicide, it is expected to be solubilized by the surfactant once CMC is exceeded. Furthermore, depending on their hydrophilicity, non-ionic surfactants have the ability to solubilize polar compounds (Xiarchos and Doulia, 2006). This hydrophilicity is known to be governed by the number of the ethylene oxide groups (EO) in the surfactant molecule, i.e., the greater the number of EO groups, the more hydrophilic the surfactant (Jafverti et al., 1994). Since Brij 35 has twenty-three EO groups, it is expected to exhibit a high capacity to solubilise polar compounds, such as metribuzin in the environment.

6.3.4. Effect of non-ionic surfactant Brij 35 on metribuzin in leachate

The leachate samples were analyzed to quantify the amount of metribuzin leaching to shallow ground water. Metribuzin concentrations in the leachate of both Brij 35 treatments, ranging from 67.22 to 23.02 μg L^{-1} for Brij 35 at 0.5 g L^{-1}, and 84.80 μg L^{-1} to below the detection limit for Brij 35 at 5 g L^{-1} (Fig. 6.8). The levels of metribuzin in the leachate were significantly greater at the treatment of Brij 35 at 5.0 g L^{-1} than Brij 35 at 0.5 g L^{-1} after the first two irrigation events. Metribuzin concentrations reached a maximum at the third application (17.19 μg L^{-1}) in the tap water leachate samples. This observation can be explained by the fact that metribuzin adsorption in sandy soil is reversible and thus residues might escape to lower layers in the soil profile (Maqueda et al. 2009). Likewise, since sandy soil possess a low CEC and large pore spaces, high leaching potential for herbicides may be observed (Aggarwal et al., 2006). However**,** in a lysimeter study, no metribuzin concentrations were detected in the leachate from a sandy soil after irrigation with either tap water or a non-ionic surfactant metabolite, NP (12 mg L^{-1}) (Nilufar, 2005).

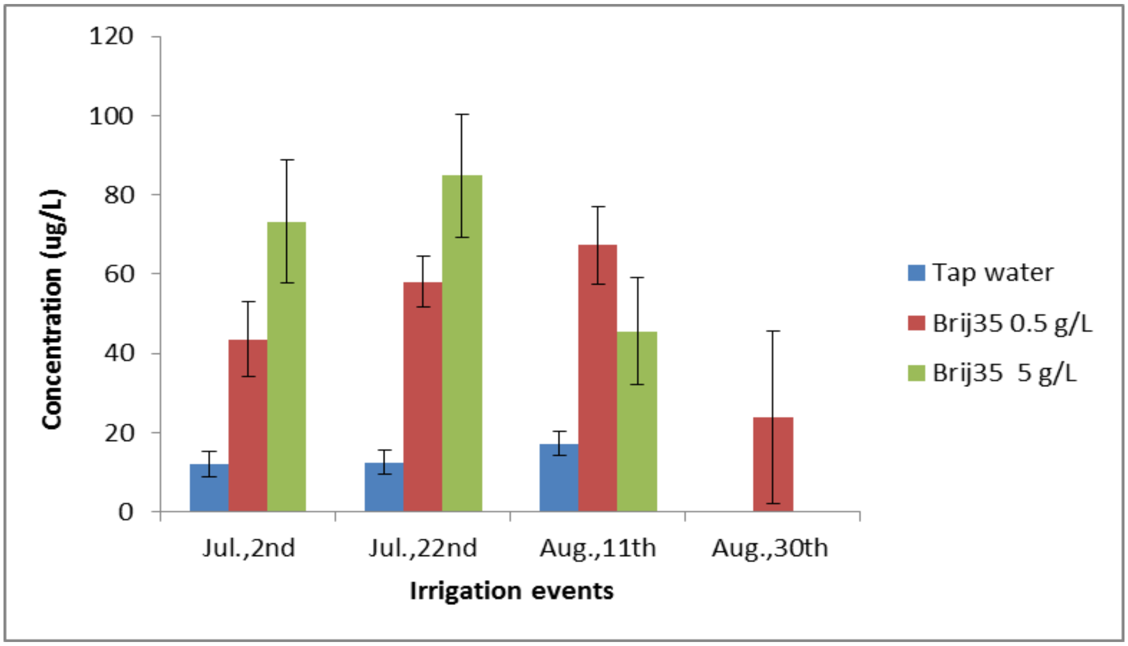

Figure 6.8 Metribuzin concentration in the leachate

In the case of surfactant treatments, the amount of metribuzin moved from the surface to the leachate in the treatment of Brij 35 at 5 g L^{-1} was 84.80 µg L^{-1} after the second irrigation event. This amount exceeded the acceptable level for metribuzin in drinking water (80 µg L^{-1}), according to Canadian guidelines (Health Canada, 2010). Generally, above the CMC, the lipophilic end (alkyl chain) of the surfactant molecule aggregate together inside the micelle, with the hydrophilic end point towards the aqueous phase on the exterior (Cheah et al., 1998). Thus, micelles enhance the solubility of low polarity organic compounds by partitioning them into the hydrophobic micelle core. Since metribuzin is a polar herbicide, it is expected to be attracted by the polar head of the surfactant by hydrogen bonding. Partitioning of pesticides with surfactants is well documented in the literature (Zimmerman et al., 1999; Kile and Chiou, 1989; Wang and Keller, 2008). More specifically, polar compounds, such as pesticides, are solubilized in the neighborhood of stern layer of the surfactant (Katagi, 2008). Additionally, non-ionic alcohol ethoxylates (AE) are found to enhance the downward movement of pesticides when applied at high (*vs.* low) concentrations to soil columns (Huggenberger et al., 1973).

Typically, sorption of herbicides onto soil surfaces occurs when the polar components in soil interact with the polar functional groups of the herbicide and since metribuzin has an amide group, interaction with polar sites may occur. However, if water is present, metribuzin tends to interact with water molecules via hydrogen bonding and form hydrophilic complexes, which in turn, facilitate the leaching process. This may explain the relationship between its solubility and leaching potential (Laird and Koskinen, 2008). Since surfactants can interact with soil, it may compete with metribuzin for available binding sites in soil. This can lead to enhancing the free downward movement of metribuzin in the soil profile. Recently, Undabeytia et al. (2011) confirmed the role of polar groups (amide) in metribuzin in the formation of water bridges via hydrogen bonding with the hydrophilic head of the non-toxic surfactant phosphatidylcholine in clay formulations. Therefore, in the presence of a non-ionic surfactant, such as Brij 35 at concentrations above its CMC, metribuzin would be captured by micelles, with its polar groups oriented toward the polar head (EO) of the micelles, which would exhibit a strong hydrophilic interaction via hydrogen bonding or dipole-dipole effects. In the present study, results of the lysimeter experiment are explained by the findings of the sorption study. This conclusion confirms the role of non-ionic surfactant Brij 35 in decreasing the sorption coefficient of metribuzin and hence promoting its release from soil. Therefore, additional research should be carried out to better understand the effect of chemical compounds when they coexist as mixtures in the environment.

Conclusions

Understanding the mobility of metribuzin within soil-water-surfactant systems is an important step in evaluating the risk resulting from irrigation with wastewater. The present study showed the presence of non-ionic surfactant (Brij 35) in concentrations higher than its CMC, increased the downward movement of metribuzin in the soil profile, presumably due to the solubilization power of micelles in the soil-water system when Brij 35 was present at 0.5 or 5 g L^{-1} or the competition between the surfactant and metribuzin for soil binding sites. Additionally, metribuzin concentrations in the leachate were higher (about 5 times) in the presence of Brij 35 compared to the tap water. In spite of the fact that metribuzin is water soluble, other lysimeter studies have shown metribuzin to rarely move below 30 cm depth in the soil profile. The present study indicates that the presence of a non-ionic surfactant in irrigation water increased the mobility of metribuzin in soil and led to its presence in leachate samples at a depth of 1 m below the soil. Therefore, the continuous use of wastewater containing non-ionic surfactants at concentrations exceeding their CMC can be expected to increase the possibility of pesticides being detected in leachate, eventually reaching ground water, and thus potentially contaminating water resources.

Chapter 7 – SUMMARY AND GENERAL CONCLUSIONS

A lysimeter study was undertaken to evaluate the effect of irrigation with non-ionic surfactant rich wastewater on the mobility of three chemicals, commonly used in agriculture: the herbicide, metribuzin, and two antibiotics, oxytetracycline and monensin. Twenty-seven lysimeters (nine for each chemical), packed with a sandy soil, were used to conduct the study. The lysimeters were covered with a rainfall shelter. To simulate a worst-case scenario, no crops were planted. The three irrigation treatments (in triplicate) consisted of tap water and water containing the non-ionic surfactant, Brij 35, at 0.5 g L^{-1} and 5.0 g L^{-1}. Soil and water samples were taken at pre-determined time intervals and were analyzed in the laboratory. A laboratory sorption study was also conducted to quantify the partition coefficient (k_d) for the tested compounds in the absence and the presence of Brij 35 at concentrations below, and above, its critical micelles concentration, CMC.

The following conclusions were drawn from this study:

Oxytetracycline: The results indicated that the greater downward movement of OTC was observed in the treatments of surfactant at concentration of 0.5 g L^{-1}. OTC was found in the leachate of all three treatments, with greater amounts recovered in the presence of the surfactant, as compared to tap water. The mass balance study revealed that after 60 days, the total OTC in the soil profile and leachate samples was 1.5 and 4 fold greater in the 5 and 0.5 g L^{-1} treatments, than in the tap water treatment, respectively. Despite the fact that OTC is immobile in soil below 5 cm, 0.76% of the applied OTC was recovered in the leachate of the lysimeters irrigated with tap water, and 6.47% and 3.86% for the 0.5 and 5.0 g L^{-1} surfactant solutions, respectively. These conclusions have been confirmed by the sorption experiments. The highest values of Freundlich sorption coefficients (K_F) were observed when the surfactant was present as monomer (below CMC at 0.02

g L^{-1}). As a result of increasing the concentration of the surfactant to 0.25 g L^{-1} (about 2.5 CMC), the K_F value decreased and by increasing the surfactant concentration to 5 g L^{-1}, a slight increase in the K_F value was observed. Furthermore, the presence of monomers in the solution enhanced the surfactant sorption onto the soil. This eventually led to more OTC sorbed to soil but once CMC was reached, micelles present in the solution appear to compete with the sorbed surfactant for OTC. The more micelles present in the aqueous phase, the more OTC partitioning into the micelles will occur, resulting in higher concentrations released from the sorbed OTC.

Monensin: The results showed that its mobility increased in the presence of the surfactant with significantly higher leaching for surfactant concentration of 5 g L^{-1}. Monensin was found in the leachate samples of the three treatments, with significant amounts recovered in the presence of surfactant, compared to tap water. The mass balance study indicated that about 0.26% of the applied monensin was recovered in the leachate of tap water, and 0.81 and 1.3%, respectively, for the 0.5 and 5.0 g L^{-1} surfactant treatments.

The sorption test indicated that the affinity of monensin to soil is inversely related to the surfactant concentration. The calculated Freundlich sorption coefficient K_F was 120.22 mL g^{-1} for the treatment of tap water then decreased to 63.09 mL g^{-1} for the surfactant concentration for 5.0 g L^{-1}. Interestingly, unlike OTC, the calculated sorption coefficient at a surfactant concentration below CMC was found to be less than the corresponding value in the absence of the surfactant; indicating the possibility of low sorption affinity to soil in the presence of monomers. Hence, this increases the risk of monensin reaching ground water at low surfactant concentrations.

Metribuzin: Results indicate that the presence of the non-ionic surfactant (Brij 35), in concentrations higher than its CMC, increased the downward movement of metribuzin in the soil profile. Compared to the tap water irrigation treatment, metribuzin concentrations in the leachate were higher in the presence of the surfactant. No significant difference on the mobility was observed, however, for the two surfactant treatments. These results were confirmed by the laboratory sorption study. Results showed that metribuzin sorption coefficient, K_d was linear with a noticeable decrease in K_d values in the presence of the surfactant. Presumably, this is due to the solubilisation power of micelles in the soil-water system when surfactant is present at concentrations 0.5 or 5 g L^{-1}.

The mass balance study revealed that after 60 days, the total metribuzin in the soil profile and the leachate was respectively 4 and 6 fold greater in the 5 and 0.5 g L^{-1} treatments, compared to the tap water treatment. Further, about 0.34% of the initially applied metribuzin was recovered in the leachate of the lysimeters irrigated with tap water, and 1.86 and 2.04% for the 0.5 and 5.0 g L^{-1} surfactant solutions, respectively.

Effect of Surfactant on Desorption of Immobile and Mobile Antibiotics:

The sorption and desorption hysteresis and partitioning of OTC and SCP in a water-surfactant soil system were investigated. Depending on the absence or the presence of the non-ionic surfactant, the sorption coefficient, K_F, value of OTC and SCP varied. The OTC sorption was high in the presence of surfactant in the monomer form; however, it decreased dramatically once micelles were present in the solution (above CMC), indicating a solubilizing effect. On the other hand, the SCP sorption coefficient increased in the presence of the surfactant in the monomeric and micelles form, indicating a higher affinity to sorb to the surfactant that might have already sorbed to soil.

Furthermore, the desorption coefficient decreased for OTC and SCP in the presence of the surfactant, with a higher efficiency coefficient for OTC when compared to SCP in the presence of surfactant depending on the water medium**.** The thermodynamic index of irreversibility, TII, showed the existence of hysteresis only in the presence of surfactant monomers for OTC. However, no hysteresis was found in the case of SCP except for the highest surfactant concentration at 5.0 g L^{-1}, indicating an irreversible effect.

Chapter 8 – CONTRIBTIONS TO KNOWLEDGE AND SUGGESTIONS FOR FURTHER RESEARCH

The following are the contributions to knowledge derived from this research:

1. To the author’s knowledge, this study represents the first attempt to evaluate the effect of a non-ionic surfactant, present in wastewater used for irrigation, on the mobility of veterinary antibiotics in soil. This study is considered as a step forward in understanding the sorption and transport of mixed chemicals since they commonly occur as mixtures in the environment. The study clearly showed significant downward movement of the tested antibiotics and herbicides in the presence of a nonionic surfactant. Therefore, the use of surfactants rich wastewaters might enhance the mobility of contaminants and increase ground water pollution.

2. Unlike, OTC and monensin, the antibiotic sulfachloropyridazine (SCP), is known to be more mobile in soil. The presence of the non-ionic surfactant (in monomers and micelles form) increased the sorption of SCP to soil, thus hindering it from moving downward. The desorption efficiency of the nonionic surfactant was also found to be higher for OTC, as compared to SCP, thus increasing its leaching potential. This indicates the importance of the antibiotic nature in the fate and transport process when it coexists with other chemicals in the environment.

3. The presence of surfactant in irrigation water may significantly increase the mobility of metribuzin in soil and confirms the possibility of greater risk of ground water pollution with pesticides from wastewater irrigation.

Suggestions for Further Research

The reuse of waste water has become a management option for many parts around the world due to water scarcity. This study was conducted successfully in the lysimeters and in the laboratory in order to evaluate the impact of the presence of non-ionic surfactants in wastewater on fate and transport of pollutants in the environment. Based on the work done in this project, the following recommendations are made for future research:

i. In the present study, the mobility of antibiotics and herbicides in the presence of a non-ionic surfactant in sandy soil was observed. However, repeating this experiment with other soil types could further improve our understanding of this problem.

ii. Non-ionic surfactants seem to be replacing the anionic surfactants in general. However, in textile industry, anionic surfactants are still used. Therefore, it is suggested to study the effect of anionic surfactants on the mobility of antibiotics and herbicides.

iii. In this present study, surfactants were added to the freshwater to simulate wastewater. In further studies, effluent from a wastewater treatment plant may be used.

iv. Although the study was conducted using three antibiotics belonging to different classes, further research may be carried out to assess the risk of applying surfactant-rich water on the mobility of other classes antibiotics and on-counter drugs.

v. Further studies are recommended for modeling the fate and transport of pollutants in the presence of surfactants. This could simulate a wide range of complex scenarios. Therefore, the aid of computer models is important to better evaluate the environmental impacts of such pollutants.

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