

# **IMIDACLOPRID SORPTION AND TRANSPORT IN CROPLAND, GRASS BUFFER AND RIPARIAN BUFFER SOILS**

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## ABSTRACT

Knowledge of neonicotinoid sorption and transport in soil is crucial to understanding environmental risk associated with the most widely used class of insecticides. To determine mobility and transport of the neonicotinoid imidacloprid (ICD), batch sorption and column leaching experiments were performed using soils collected from cropland (crop), grass vegetative buffer strips (VBS), and riparian VBS. Single-point, solid-to-solution partition coefficients ( $K_d$ ) were determined by reacting soil collected from the vegetation treatments at six sites with radiolabeled ( $^{14}\text{C}$ ) ICD. For the column experiments, soils from the three vegetation treatments collected at one site were packed into individual glass columns and water flow was characterized by applying  $\text{Br}^-$  as a nonreactive tracer. A single pulse of  $^{14}\text{C}$ -ICD was applied, and ICD leaching was monitored for up to 45 days. Bromide and ICD breakthrough curves for each column were simulated using CXTFIT, a convection/dispersion-based transport equilibrium model, and HYDRUS-1D, a multisite sorption chemical non-equilibrium transport model. Sorption results indicated that ICD sorbs more strongly to soil from riparian VBS ( $K_d = 22.6 \text{ L kg}^{-1}$ ) than crop ( $K_d = 11.3 \text{ L kg}^{-1}$ ;  $p = 0.04$ ) and soil organic carbon (OC) was the strongest predictor of ICD sorption ( $p < 0.0001$ ). The column transport study found peak concentrations of ICD at 5.83, 10.84 and 23.8 pore volumes for crop, grass VBS, and riparian VBS, respectively. HYDRUS-1D results indicated that the two-site, one-rate linear reversible model best-described results of the breakthrough curves, indicating the complexity of ICD sorption and demonstrating its mobility in soil. Greater sorption and longer retention by the grass and riparian VBS soil compared to the crop soil suggests that VBS may be a viable means to mitigate ICD loss from agroecosystems.

# Chapter 1.0 Introduction

## 1.1 Introduction

Neonicotinoids are a class of insecticides used to combat a broad spectrum of sucking and chewing pests (Jeschke et al., 2011). Imidacloprid (ICD), the most used insecticide, is included in the chemical class of neonicotinoids (Buchholz et al., 2002). Effectiveness of neonicotinoids is due to their systemic nature, allowing for plant uptake and xylem mobility, and ability to control a broad spectrum of pests while being less toxic to mammals than previously used insecticides (Buckingham, 1997). Insects are exposed to neonicotinoids from consuming part of a treated plant, including pollen. Neonicotinoid application techniques, such as seed coating or foliar spray, to agricultural fields alter its fate and transport in soil (Jepson et al., 2011). Seed coatings, a preventative pest control technique, treated 30% of all *Glycine max* (soybean) seeds and 79% of *Zea mays* (corn) seeds in 2011 (Douglas et al., 2014).

The chemical characteristics of ICD dictate fate and transport in the environment. The chemical has high solubility ( $610 \text{ mg L}^{-1}$ ) in water resulting in a great potential to leach through soil and impact untargeted aquatic organisms (Fossen, 2006). However, its ability to strongly sorb to fine textured or high organic carbon soils combined with its long half-life results in accumulation in soils at concentrations reaching  $100 \text{ } \mu\text{g kg}^{-1}$  (Bounmatin et al., 2014). Imidacloprid uptake in cropland soil has been reported to be as low as 5%, indicating that the bulk of added ICD remains in soil where it can accumulate (Goulson et al., 2014). Therefore, the fate and transport of ICD in soils under different management treatments must be further evaluated.

Several studies cite soil carbon as the most significant predictor of ICD sorption and retention (Broznic et al, 2012; Cox et al, 1998; Koskinen et al, 2000). Vegetative buffer strips

(VBS) are rows of perennial vegetation, consisting of grasses, shrubs, trees or a combination of species, surrounding agricultural land or lining stream banks (Schultz et al., 1995) can help mitigate non-point source agrochemical transport (Lowrance et al., 1997) via physical, chemical and biological mechanisms. Vegetative buffer strips enhance runoff infiltration and trap sediment (Lin et al., 2011), increase agrochemical sorption often due to greater soil organic carbon content (Chu et al., 2012), and reduce contaminant toxicity through plant and microbial metabolism of organic pollutants (Mandelbaum et al., 1995). The retention and degradation of ICD in VBS soil could prevent exposure to untargeted organisms and minimize ICD contamination of surface and drinking waters; however, previous studies have not evaluated the potential for VBS to alter ICD fate and transport in soil.

## **1.2 Objectives**

The overall objective of this research is to enhance our understanding of ICD sorption and transport in soils planted to row-crops and VBS. The specific objectives and hypotheses of this research are as follows:

***Objective 1.*** Determine the sorption of ICD by measuring the partition coefficient ( $K_d$ ) values of soil collected from three different vegetative management treatments planted to cropland, grass VBS, and riparian VBS.

***Hypothesis 1.*** The presence of soil organic carbon (OC) will increase ICD sorption due to greater chemical reactivity. Grass and riparian VBS soil will contain greater OC than cropland soil due to differences in the amount of residues deposited on the soil surface and greater root turnover associated with perennial vegetation. In turn, the grass and riparian VBS soil will have a greater  $K_d$  values than the cropland soils.

**Objective 2.** Study differences in ICD leaching through columns packed with soil from the three different vegetative treatments.

**Hypothesis 2.** Greater ICD mass will be recovered in the leachate fraction of cropland soil due to lesser ability of this soil to sorb ICD. Imidacloprid mass recovery in the leachate fractions of columns packed with grass and riparian VBS soils will be reduced due to greater sorption to these soils.

**Objective 3.** Determine transport and sorption mechanisms of ICD in soil collected from the three different vegetative treatments using an inverse computer modeling technique.

**Hypothesis 3.** The soil planted to grass and riparian VBS soil will have a greater fraction of irreversible sites due to a greater amount of OC coating external surface area of the soil. In addition, structure and texture differences will result in a more torturous pathway for ICD. The cropland soil will have a greater fraction of instantaneous sites due to less soil OC.

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## Chapter 2.0 Literature Review

### 2.1 Use of Neonicotinoids in Agriculture

Neonicotinoids are a class of insecticide used to combat a broad spectrum of sucking and chewing pests (Jeschke et al., 2011). From the 1970s to the 1990s organophosphates, carbamates and synthetic pyrethroids dominated the insecticide market (Maienfisch et al., 2001). Prior to this, alkaloid (S)-nicotine, derived from tobacco plants, had been used as a natural insecticide. The first neonicotinoid, imidacloprid (ICD), was released in 1991 by Bayer Crop Science (Kollmeyer et al., 1999). In 2009, ICD accounted for 41.5% of the market with a value of \$2.6 billion and it is approved for use in 120 different countries and 140 crops, including corn, soybean, *Gossypium hirsutum* (cotton), *Oryza sativa* (rice), *Solanum tuberosum* (potato), *Beta vulgaris* (sugar beet), vegetables, and pome and stone fruits (Jeschke et al., 2011). Currently, there are seven neonicotinoids on the market, acetamiprid, clothianidin, dinotefuran, ICD, nitenpyram, thiacloprid, and thiamethoxam (Tomizawa and Casida, 2005).

Neonicotinoids are the first synthetic insecticide to target the nicotinic acetylcholine receptors (*nAChR*) in the central nervous system (Buckingham et al., 1997). Their systemic nature allows for plant uptake and xylem mobility within the plant, including pollen and reproductive parts, protecting the entire plant from insects (Buchholz and Nauen, 2002). Insects are exposed to the potent neonicotinoids from pollinating or consuming portions of the treated plant. Neonicotinoids accumulate on the *nAChR* and, at low doses, the insecticides cause nervous stimulation (Goulson et al., 2014). At high doses, receptor blockage occurs potentially leading to paralysis or death. Neonicotinoids are believed to be more toxic to invertebrates than

vertebrates, because they bind more effectively to insect *nAChR* and vertebrates have fewer *nAChR* (Tomizawa and Casida, 2005).

Imidacloprid coated seeds and foliar spray are the two most common application techniques used in agriculture (Jepson et al., 2011). Seed coatings are a preventative pest control technique, and 30% of all soybean seeds and 79% of corn seeds were coated with neonicotinoids as of 2011 (Douglas et al., 2014). Corn seeds are often coated with  $>3$  g active ingredient  $\text{kg}^{-1}$  (Munkvold et al., 1996). Studies have reported low amounts of ICD uptake by crops. For example, uptake by soybean accounted for  $\sim 5\%$  of applied neonicotinoids (Goulson et al., 2014) and uptake by *Helianthus annuus* (sunflowers) was  $<10\%$  of applied ICD (Laurent et al., 2003). The remaining compound resides on soil particles, in soil solution or is leached from the soil (Goulson et al., 2014). Foliar spray of ICD is more commonly used for nut and fruit trees in response to an insect outbreak, as opposed to a preventative measure (Jepson et al., 2015).

## **2.2 Presence of Neonicotinoids in the Environment and Potential Environmental Hazards**

High sorption values and a long half-life can expose untargeted organisms to ICD. Due to the systemic nature of neonicotinoids, *Bombus terrestris* (bumble bee) and *Apis mellifera* (honey bee) are exposed to neonicotinoids through nectar and pollen of flowering crops, which has been linked to population reduction (Henry et al., 2012; Whitehorn et al., 2012). Whitehorn et al. (2012) found that bumble bee colonies treated with the neonicotinoid ICD in pollen and sugar water containing  $6 \mu\text{g kg}^{-1}$  and  $0.7 \mu\text{g kg}^{-1}$ , respectively, resulted in an 85% reduction of new queens compared to control colonies, and colonies treated with ICD significantly decreased in weight compared to control colonies. Henry et al. (2012) found that the homing ability of honey

bees decreased for bees treated with a nonlethal dose of the neonicotinoid thiamethoxam, as compared to non-treated bees, and the risk of death while foraging was doubled.

Movement of neonicotinoids through the food chain is also of environmental concern. Douglas et al. (2014) found evidence of the neonicotinoid thiamethoxam harming insects beneficial to crops, moving up the food chain, and reducing crop densities. After feeding on soybeans planted with thiamethoxam-coated seed, *Deroceras reticulatum* (slug pest) was unaffected. However, greater than 60% of *Chlaenius tricolor* (predaceous beetles) became impaired after feeding on the slug pests, providing evidence of thiamethoxam transfer through the food chain. Crop density was reduced up to 19% due to greater damage of soybeans by slugs in absence of predaceous beetles; thus, indicating neonicotinoids may not be economically advantageous for soybean production.

In regions where neonicotinoids are used, insectivorous birds and mammals may experience food deprivation due to a decrease in invertebrate densities. Hallmann et al. (2014) found population declines for 10 insectivorous bird species were associated with greater surface-water ICD concentrations in the Netherlands. When surface-water ICD concentrations were  $19.43 \pm 0.03 \text{ ng L}^{-1}$ , bird populations decreased by 3.5% per year. Quantifying ICD fate and transport in soils under different land uses is crucial to understanding ICD bioavailability to untargeted organisms, yet information on the subject is very limited.

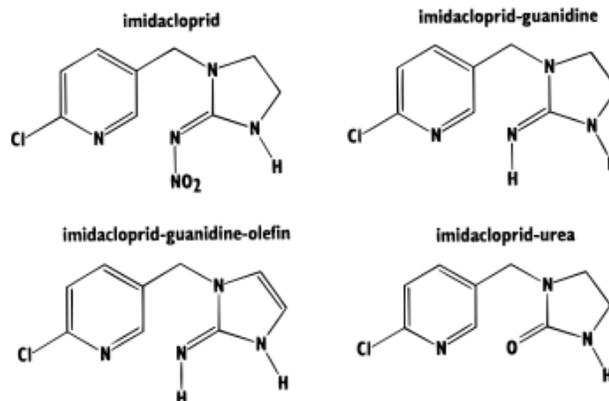
### **2.3 Utilizing Vegetative Buffers to Mitigate Pollutant Transport**

Vegetative buffer strips (VBS) can mitigate non-point source agrochemical pollutant transport (Lowrance et al., 1997). Vegetative buffer strips are defined as rows of vegetation, consisting of grasses, shrubs, trees or a combination of species, surrounding agricultural land or lining stream banks (Schultz et al., 1995). Pollutant transport into waterways is reduced by VBS

through physical, chemical and biological mechanisms. Physically, VBS enhance runoff infiltration and trap sediment (Lin et al., 2011). Chemically, agrochemicals typically exhibit greater  $K_d$  values for VBS soils (Chu et al., 2012), resulting in a lower concentration of agrochemicals in runoff leaving the VBS (Lin et al., 2011). Biologically, microbial activity and biomass have been reported to be greater in VBS soil compared to cropland or bare soil (Lin et al., 2003; Lin et al., 2011), leading to faster and more complete degradation of organic pollutants (Mandelbaum et al., 1995; Lin et al., 2008; Lin et al., 2011b). Plant uptake of neonicotinoids in wetlands has also been observed (Main et al., 2015). Currently, there are no studies investigating neonicotinoid sorption or degradation within VBS. However, previous studies have observed greater  $K_d$  values for neonicotinoids when the insecticide is reacted with soils containing greater amounts of carbon (Rodriguez-Liebana et al., 2012 and Cox et al., 1998). Vegetative buffer strips typically containing greater soil organic carbon concentrations (Mandelbaum et al., 1995); therefore, VBS have the potential to mitigate neonicotinoid transport.

## 2.4 Previous Studies Investigating Imidacloprid Behavior in Soil

Imidacloprid,  $C_9H_{10}ClN_5O_2$ , is a polar organic compound defined by the structure in Figure 2.1 (Cox et al., 1997). There are multiple pathways for ICD degradation that result in the formation of common ICD metabolites: ICD-guanidine; ICD-guanidine-olefin; and ICD-urea (Sur, 2003). To form ICD-guanidine, the  $NO_2$  group is reduced to an amine (Broznic et al., 2011); this is a commonly observed reaction for organic

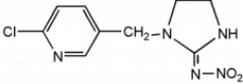


**Figure 2.1** Imidacloprid and metabolite structures (Cox et al. 1997).

contaminants with  $NO_2$  groups such as dinitroaniline herbicides and the common explosives, TNT (trinitrotoluene) and RDX (trinitrotriazine) (Golab et al., 1979; Han, 2010). The loss of NH replaced by O results in the formation of ICD-urea (Sur, 2003). To form ICD-guanidine-olefin, the imidazolidine ring undergoes hydroxylation (Broznic et al., 2011).

The systemic nature of ICD is due to high solubility in water ( $514 \text{ mg L}^{-1}$ ) (Fossen, 2006). Due to the polar structure of ICD, hydrogen bonding with water could occur with the hydrogen molecule in the amine ring or an oxygen molecule on the nitro group. If the chloride on the imidazolidine ring becomes deprotonated, it has the potential to be water soluble (Morgan, 2011).

**Table 2.1** Selected properties of imidacloprid<sup>a</sup>.

| Molecular Structure   | Molecular Weight<br>g mol <sup>-1</sup> | S <sub>w</sub> <sup>b</sup><br>mg L <sup>-1</sup> | GUS         | Log K <sub>ow</sub> <sup>d</sup> | pK <sub>a</sub> <sup>e</sup> |
|---|---|---|-------------|----------------------------------|------------------------------|
|  | 255.7                                   | 514   | 3.76 (High) | 0.57                             | 1.56, 11.2                   |

<sup>a</sup>Data were obtained from Chamberlain et al. (1996); PPDB (2014) and Fossen (2006).

<sup>b</sup>S<sub>w</sub>, water solubility.

<sup>c</sup>GUS, Groundwater Ubiquity Score.

<sup>d</sup>K<sub>OW</sub>, octanol-water partition coefficient.

<sup>e</sup>pK<sub>a</sub>, acid dissociation constant.

#### 2.4.1 Factors affecting Imidacloprid persistence in soil

Microorganisms, pH and moisture conditions directly control the rate of ICD degradation in soil, often measured by the half-life. The half-life of ICD varies greatly among studies.

Baskaran et al. (1999) found ICD's half-life in soil to be 990, 1080 and 1230 days, resulting in 37% to 40% of applied ICD being degraded in 24 months. In contrast, Sarkar et al. (2001) found the half-life of ICD to range from 36.4 to 43.7 days. The half-life of ICD decreased by 50% in anoxic soil conditions compared to oxic conditions (Herner et al., 2014), indicating more rapid degradation under anoxic conditions. In addition, 22.5% of ICD had degraded in unsterilized soils, while 0% of ICD had degraded in sterilized soil after 25 days (Liu et al., 2011). However, more research should be conducted to understand environmental variables impacting ICD degradation.

Despite the variability in reported ICD soil degradation, ICD clearly has the potential to persist and potentially accumulate in some environments. In such cases, frequent applications do not allow for dissipation to fully occur (de Perre et al., 2014). The concentration of ICD in fields after planting ICD-coated seeds ranged from less than 0.09 and 10.7 µg kg<sup>-1</sup> (Jones et al., 2014).

In the top 10 cm of the soil, ICD concentrations ranged from 17.5 to 59.6  $\mu\text{g kg}^{-1}$  after 4 years of applying 133 g ICD  $\text{ha}^{-1}$  (Anon, 2006). Bonmatin et al. (2014) reported ICD concentrations of  $<1 \mu\text{g kg}^{-1}$  to  $>100 \mu\text{g kg}^{-1}$  extracted from French farmland soil. Due to the high variability in the half-life, persistence and accumulation of ICD in soils, ICD is of environmental concern.

Greater soil organic carbon increases ICD sorption parameters and microbial activity. In turn, microbial activity can decrease ICD persistence in soil. The addition of organic carbon to aerated soil via compost application (i.e., composted horse manure, vegetable waste, and leaves and grass) decreased ICD half-life from  $> 60$  days to 36 days (Herner et al., 2014). The half-life of thiamethoxam decreased in an aqueous solution of ultrapure water from 18.7 hours to 13.7 hours after wastewater was added (Peña et al., 2010).

#### 2.4.2 Sorption concepts and terminology

Pollutant sorption studies involve reacting a known amount of compound with a fixed soil mass and volume of solution for a specific period of time at a constant temperature. Upon completion, the compound of interest in solution is measured in comparison to blank samples (i.e., no soil). The following equation can be used to calculate the amount of compound sorbed:

$$q_{ads} = \frac{(C_{ads,B})(V_B) - (C_{ads,S})(V_S)}{m_s} \quad [1]$$

Where  $q_{ads}$  is the surface excess of ICD (i.e., amount sorbed) after the reaction period ( $\text{mmol kg}^{-1}$ ),  $C_{ads,B}$  and  $C_{ads,S}$  are the equilibrium compound concentrations ( $\text{mmol L}^{-1}$ ) in blank (B) and samples (S) after reaction,  $V_B$  and  $V_S$  are the volume of solution (L) added to the blanks and samples, and  $m_s$  is the mass of soil (kg) added to the reaction vessel (Essington, 2004).

The solid to solution partition coefficient,  $K_d$ , is calculated using the following equation:

$$K_d = \frac{q_{ads}}{C_{ads,S}} \quad [2]$$

Where  $q_{ads}$  is the concentration of analyte sorbed to soil and  $C_{ads,S}$  is the concentration of analyte remaining in solution after reaction. The solid to solution partition coefficient values are often indicative of a compound's mobility in the soil environment. Thus,  $K_d$  serves as an important parameter for computer models predicting a compound's environmental behavior (Essington, 2004).

### 2.4.3 Sorption of Imidacloprid to soil

The leaching potential of a compound to surface or groundwater systems is largely influenced by its sorption to soil. Soil properties, such as organic carbon content, texture, cation exchange capacity (CEC), and pH, can have a significant impact on ICD sorption to soil. The ability of a compound to sorb to soil is also dependent upon the soil organic carbon-solution partition coefficient value ( $K_{OC}$ ) (Cox et al., 1997). The  $K_{OC}$  value of ICD is reported to be 132 to 310 L kg<sup>-1</sup> (Table 2.1) (Fossen, 2006; PPDB, 2014), indicating it is moderately mobile in the soil environment.

Many studies agree that soil organic matter content (SOM) or organic carbon content (OC) is the strongest predictor of ICD sorption (Cox et al., 1998, Fernández-Pérez et al., 1998, Liu et al., 2011, Broznic et al., 2011). Fernández-Pérez et al. (1998) conducted a batch sorption experiment on peat, native soil, amended soil and sand. They observed ICD  $K_d$  values ordering from peat > native soil > amended soil > sand. Organic matter and cation exchange capacity were found to have the greatest positive correlation with ICD  $K_d$  values. Upon completion of an ICD sorption experiment six different soils, Liu et al. (2011) found percent SOM was the most significant predictor of ICD Freundlich sorption capacity coefficient,  $K_f$ , values in a linear

regression analysis. Percent clay, pH and CEC were also included in the model. In addition, Broznic et al. (2011) conducted a linear regression analysis upon completion of an ICD sorption experiment of six different soils. However, they partitioned SOM into percent OC, percent humic acid and percent fulvic acid. Percent OC was the most significant predictor of ICD  $K_f$  values. Cation exchange capacity and percent clay were also found to be significant predictors with positive correlations.

In addition, Cox et al. (1998) reported that ICD  $K_f$  values decreased after the removal of soil organic matter (SOM) on clay minerals via  $H_2O_2$ . This implies that SOM enhances ICD sorption to a greater extent than soil minerals. As organic carbon content increased in soil, the  $K_f$  value for ICD and metabolites increased (Cox et al., 1997). Ping et al. (2010) evaluated the impact of exogenous humic acid additions to soil on ICD  $K_f$  values. They observed that the addition of humic acid (HA) to soil increased ICD  $K_f$  values, and the authors attributed this effect to HA increasing the soil surface area and providing additional hydrophobic sites for ICD adsorption. Similar results were found by Cox et al. (1998). However, Cox et al. (1998) also observed the addition of fulvic acid decreased ICD  $K_f$  values, thus increasing ICD leaching potential. Therefore, different characteristics of SOM can alter ICD sorption values. Similar results were found by Flores-Cespedes et al. (2002). In addition, a positive relationship between soil organic carbon (%) added via sewage sludge and ICD  $K_d$  values were observed (Rodríguez-Liébana et al., 2012). Several studies report CEC also increases reactivity of the soil surface, and CEC is often the second strongest predictor of ICD sorption values (Cox et al., 1998b, Liu et al., 2006, Broznic et al., 2011). Broznic et al. (2011) observed a significant correlation between CEC and percent OC.

Many studies agree that soil texture is a significant predictor of ICD sorption values (Cox et al., 1997, Cox et al., 1998, and Jeong et al., 2011). For example, Jeong et al. (2011) reported that solid-solution partition coefficient values of ICD increased as soil texture became more fine with  $K_d$  values of 2.5, 3.3, 3.67, and 7.0 L kg<sup>-1</sup> for silt loam, silty clay loam, clay loam and clay, respectively. Cox et al. (1998) removed SOM via H<sub>2</sub>O<sub>2</sub> and conducted sorption experiments to determine soil clays relationship with ICD sorption values. Amount of ICD applied to soil alters ICD sorption values (Cox et al., 1997). For example, Cox et al., (1997) reported the ICD  $K_d$  in a silt loam ranged from 1.4 to 14.4 mL g<sup>-1</sup> and the  $K_d$  values decreased as the amount of ICD applied was increased, indicating over application of ICD could lead to ICD soil leaching.

The acid dissociation constant ( $pK_a$ ) value of ICD is 11.2 and associated with the amino group (-NH). Subsequently, this results in the neutral molecule dominating ICD speciation in soil (Liu et al., 2002). Several studies observed a negative correlation between soil pH and ICD sorption values. Ping et al. (2010) adjusted soil pH to 4.5, 6.0 and 7.5 and conducted ICD sorption batch experiments. The soil pH of 4.5 resulted in the largest  $K_f$  values, followed by 6.0 and 7.5. They attributed these results to a greater pH values increasing the polarity of the soil and the electrostatic interaction between ICD and soil particles. Cox et al. (1998) found similar results. However, several studies found pH to be an insignificant predictor of ICD sorption values (Cox et al., 1998b and Broznic et al., 2011). Broznic et al. (2011) attributed a lack of pH effect on sorption to the fact that the soils studied had pH values less than the  $pK_a$  of 11.2 for ICD.

Research conducted on the relationship between temperature and ICD sorption values observed a negative relationship with ICD sorption values. Ping et al. (2010) investigated ICD

sorption at 15°C and 25°C. Imidacloprid  $K_f$  values were greatest at 15°C. They attribute these results to the increased solubility of ICD at elevated temperature (Kong et al., 2008).

Complexation of ICD with organic matter and clays likely occurs via cation exchange, water bridging, hydrogen bonding or Van der Waals interactions, although cation exchange is the most likely mechanism due to protonation of the NH group at the soil surface (Cox et al., 1998). In addition, Liu et al. (2002) obtained IR spectra after ICD sorption on Ca-clay and humic acid-clay mixtures. Subsequently, they predicted hydrogen bonds form between N=N on the imidazolidine ring of ICD and the hydrated cations of clay minerals (Figure 2.2a) or humic acids (Figure 2.2b), coordination bonds between the C=N group in pyridine ring and the exchangeable cation of clay (Figure 2.2c), and the formation of a hydrogen bond between the C=N group and a hydroxyl on the surface of HA (Figure 2.2d).

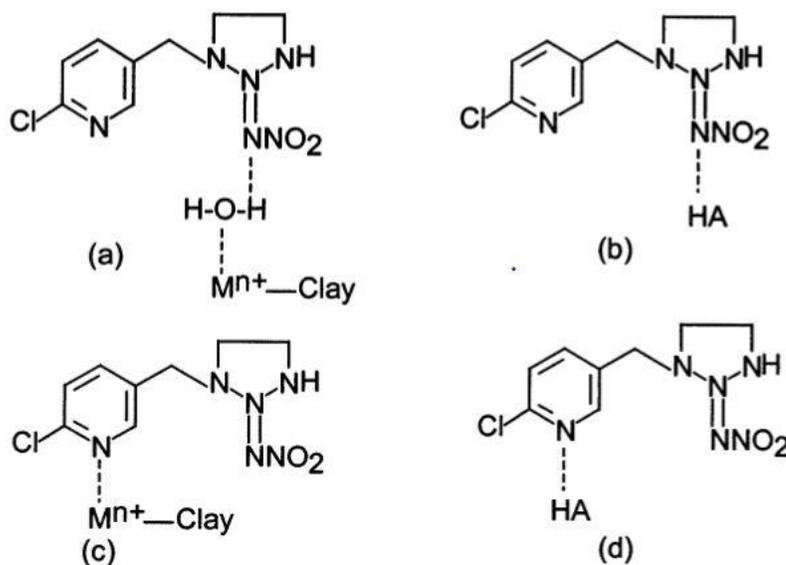
**Table 2.2** Reported imidacloprid  $K_d$  values with soil type, OC and  $K_{OC}$  from literature review.

| Study                  | Soil Texture          | OC <sup>a</sup><br>% | $K_{OC}$ <sup>b</sup> | $K_d$ <sup>c</sup><br>L kg <sup>-1</sup> |
|------------------------|-----------------------|----------------------|-----------------------|--|
| PPDB (2014)            |                       |                      | 225                   |  |
| Fossen (2006)          |                       |                      | 132-310               | 0.956-4.18                               |
| Cox et al. (1997)      | Silt loam             | 1.8                  | 78-802                | 1.4-14.4                                 |
|                        | Clay loam             | 4.1                  | 81-1560               | 3.9-64.0                                 |
|                        | Sandy loam            | 1.4                  | 71-893                | 1.0-12.5                                 |
| Jeong et al. (2011)    | Fine silty            |                      |                       | 2.491                                    |
|                        | Coarse silt over clay |                      |                       | 3.265                                    |
|                        | Very fine clay        |                      |                       | 3.663                                    |
|                        | Clay                  |                      |                       | 7.049                                    |
| Oliveria et al. (2010) | Loamy sand            | 1.45                 | 799                   | 11.3                                     |
|                        | Clay                  | 0.35                 | 158                   | 0.55                                     |
|                        | Clay                  | 2.78                 | 186                   | 5.18                                     |
|                        | Sand                  | 0.58                 | 203                   | 1.18                                     |
|                        | Sandy loam            | 7.45                 | 227                   | 16.9                                     |
|                        | Sandy clay loam       | 1.74                 | 620                   | 10.8                                     |

<sup>a</sup>OC, organic carbon.

<sup>b</sup> $K_{OC}$ , organic carbon-solution partition coefficient value.

<sup>c</sup> $K_d$ , solid to solution partition coefficient.

**Figure 2.2** Predicted adsorption mechanisms of imidacloprid to clay and humic acids (Liu et al., 2002).

## **2.5 Column Transport Experiments and Non-Equilibrium Modeling**

### **2.5.1 Column transport methodology**

Column leaching experiments are often utilized to determine the leaching potential of pollutants from soil to groundwater and surface waters. For simplicity's sake, column experiments often utilize intact or repacked columns under steady-state flow conditions. While intact columns are more representative of field conditions preserving the natural soil structure (McMahon and Thomas, 1974), preferential flow may occur due to less homogeneous soil. This will mask the chemical behavior of the compounds of interest. Repacked columns are less representative of field conditions, but are more homogeneous and reduce preferential flow (Dousset et al., 2007). To check for preferential flow a column is irrigated with bromide, a nonreactive tracer, and leachate fractions are collected for a certain interval of time (Chu et al., 2012). Finally, a solute of interest is leached through the column with irrigation of water.

Leachate concentration plotted against time creates breakthrough curves (BTC). The computer programs CXTFIT (Toride et al., 1995) and HYDRUS-1D (Šimunek et al., 2009) can estimate transport and reaction parameters using an inverse modeling technique. Multiple iterations of the model parameters are determined until the non-linear least-squares optimization is achieved. This information can help to predict field situations from laboratory-determined data. Several studies using this technique have investigated the fate and transport of organic pollutants, such as veterinary antibiotics (Chu et al., 2012), hormones (Casey et al., 2005), and herbicides and pesticides (Chen and Wagenet, 1997; Fortin et al., 1997; Tao et al., 2009).

### **2.5.2 Chemical non-equilibrium transport model**

Several chemical non-equilibrium models exist; the two-site being used most frequently. The two-site models allow for instantaneous Type 1 adsorption sites in equilibrium and first-

order kinetic Type 2 adsorption sites (van Genuchten and Wagenet, 1989; Hendrickx et al., 2002):

$$S = S_1 + S_2 \quad [3]$$

$$S_1 = f K_d C \quad [4]$$

$$\frac{dS_2}{dt} = \alpha_2 [(1 - f)K_d C - S_2] \quad [5]$$

where  $C$  is the solute concentration, ( $M L^{-3}$ );  $q$  is the water flux density ( $L T^{-1}$ );  $\theta$  is the volumetric water content ( $L^3 L^{-3}$ ), which is equal to porosity for saturated experiments;  $f$  is the fraction of Type 1 sorption sites at equilibrium;  $\alpha$  is the first-order sorption kinetic rate ( $T^{-1}$ );  $K_d$  is the empirical distribution coefficient; and the subscripts 1 and 2 represent equilibrium and kinetic adsorption sites, respectively.

The software HYDRUS-1D employs multi-site sorption concepts such as kinetic, irreversible and attachment-detachment processes allowing for estimation of chemical non-equilibrium transport parameters (Wehrhan et al., 2007).

### 2.5.3 Transport of Imidacloprid in soil

Several factors impact the transport of ICD in soil, one being SOM. Fernández-Pérez et al., (1998) observed ICD transport for 8 days in a layered soil column containing 20 cm of native soil below 20 cm of amended soil below 2 cm of peat and 8.5 cm of sand on top. They observed 95.33% of ICD remained in the soil, whereas 2.9% of ICD was detected in leachate. Of the ICD found in the soil, peat contained 92.5%, native soil contained 14.62%, amended soil contained 0.8% and sand contained 0.22%. They attributed this to the greater  $K_d$  values from greater SOM content; peat being the greatest, followed by native soil, amended soil and sand. Similar results were found by González-Pradas et al. (1999). In comparison, Gupta et al. (2002) conducted a soil column ICD leaching experiment with a sandy loam containing only 0.86% SOM. Ten grams of

ICD treated soil was placed on top of the 25 x 7 cm column. After flushing column with 2.5 L water, 28.7% of recovered ICD was present in the leachate. The majority of ICD remaining in the column was found in the bottom half of the soil. The difference in percent SOM and ICD recovered in leachate between Fernández-Pérez et al. (1998) and Gupta et al. (2002) suggest more research needs to be conducted to understand this relationship.

Vegetation has been observed to reduce ICD mobility (Peterson, 2007). Soil columns treated with ICD and seeded with or without Bermuda grass seed were watered once a week to stimulate a 2.5 cm rainfall event for 2.5 years. Extractable ICD was observed at a greater concentration throughout the experiment in vegetated columns compared to control columns at all depths (0- to 60-cm) with the exception of month 0 and 7.5- to 15-cm from months 6 to 9. They attributed this to the reduction of soil moisture in the vegetated soil columns; however, they did not investigate plant uptake of ICD or difference in SOM contents.

Time-dependent sorption of ICD has been observed in several studies (Oi, 1999; Walker et al., 1995). Oi (1999) mixed and incubated ICD soil for 0, 2, 7, 14, 28, 42, 56 and 100 days, then packed soil into columns and conducted a leaching experiment. The amount of ICD in the soil as determined by monitoring of ICD lost via leaching in a sandy loam and a silt loam decreased from 81.3% (day 0) to 41.0% (day 100) and 92.8% (day 0) to 54.5% (day 100), respectively. This was attributed to the increase in ICD  $K_{OC}$  values with increasing incubation time. In addition, as the concentration of applied ICD increases, the slope of desorption and hysteresis increases, increasing leaching potential (Cox et al., 1997).

Rômulo Penna et al. (2004), monitored ICD transport in a Dutch clay soil planted to winter wheat (*Triticum aestivum* L.) for one year. After 117 days after application most ICD remained in the top 10 cm of the soil profile. In addition, ICD concentration in 10- to 20-cm soil

layer was approximately five times less than the 0- to 10-cm soil layer. Imidacloprid concentration increased in the 10- to 20-cm layer, but remained in the greatest concentration in the 0- 10-cm layer after 189 days. On day 328, ICD concentration was greatest in the 10- to 20-cm layer. They attribute the downward movement of ICD to the plowing of the soil and concluded conducting individual column leaching experiments would better reveal ICD leaching characteristics. To date no ICD soil column leaching experiments have employed the HYDRUS 1D model.

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## Chapter 3.0 Imidacloprid Sorption and Transport in Cropland, Grass Buffer and Riparian Buffer Soils

### Abstract

Knowledge of neonicotinoid sorption and transport in soil is crucial to understanding the environmental risk associated with the most widely used class of insecticides. To determine mobility and transport of the neonicotinoid imidacloprid (ICD), sorption and column leaching experiments were performed using soils collected from cropland (crop), grass vegetative buffer strips (VBS), and riparian VBS. Single-point, solid-to-solution partition coefficients ( $K_d$ ) were determined by reacting soil collected from the vegetation treatments at six sites with radio-labeled ( $^{14}\text{C}$ ) ICD. For the column experiments, soils from the three vegetation treatments collected at one site were packed into individual glass columns and water flow was characterized by applying  $\text{Br}^-$  as a nonreactive tracer. A single pulse of  $^{14}\text{C}$ -ICD was applied, and ICD leaching was monitored for up to 45 days. Bromide and ICD breakthrough curves for each column were simulated using CXTFIT, a convection/dispersion-based transport equilibrium model, and HYDRUS-1D, a multisite sorption chemical non-equilibrium transport model. Sorption results indicated that ICD sorbs more strongly to soil from riparian VBS ( $K_d = 22.6 \text{ L kg}^{-1}$ ) than crop ( $K_d = 11.3 \text{ L kg}^{-1}$ ;  $p = 0.04$ ) and soil organic carbon was the strongest predictor of ICD sorption ( $p < 0.0001$ ). The column transport study found mean peak concentrations of ICD at 5.83, 10.84 and 23.8 pore volumes for crop, grass VBS, and riparian VBS, respectively. HYDRUS-1D results indicated that the two-site, one-rate linear reversible model best-described results of the breakthrough curves, indicating the complexity of ICD sorption and demonstrating its mobility in soil. Greater sorption and longer retention by the grass and riparian VBS soil

compared to the crop soil suggests that VBS may be a viable means to mitigate ICD loss from agroecosystems.

### 3.1 Introduction

Current agriculture practices are dependent on a class of insecticides, the neonicotinoids. Approximately 907 metric tons of imidacloprid (ICD), clothianidin and thiamethoxam were applied to 58 million ha of U.S. lands in 2008 (Pilatic, 2012). These chemicals are valued for their low mammalian toxicity (Tomizawa and Casida, 2005), versatility of application (Jeschke et al., 2010), and systemic nature which is facilitated by root uptake and xylem mobility translocating the insecticide throughout the entire plant, including pollen (Buchholz and Nauen, 2002). While human exposure to insecticides has decreased due to use of seed coat application, untargeted organisms, such as the *Bombus terrestris* (bumble bee) and *Apis mellifera* (honey bee) (Henry et al., 2012; Whitehorn et al., 2012), *Chlaenius tricolor* (predaceous beetles) (Douglas et al., 2014), and insectivorous birds (Hallmann et al., 2014) have been negatively impacted by neonicotinoids.

Time between planting seasons is not adequate for the neonicotinoids to fully dissipate from the soil (de Perre et al., 2015). Several studies have observed ICD accumulation in soil (Bonmatin et al., 2005; Anon, 2006; Jones et al., 2014). The concentration of ICD in fields after the planting of neonicotinoid-treated seed ranged from less than 0.09 to 10.7  $\mu\text{g kg}^{-1}$  (Jones et al., 2014). In the top 10 cm of the soil, ICD concentrations ranged from 17.5 to 59.6  $\mu\text{g kg}^{-1}$  after 4 years of applying 133 g ICD  $\text{ha}^{-1}$  (Anon, 2006). Bonmatin et al. (2005) reported ICD concentrations of  $<1 \mu\text{g kg}^{-1}$  to  $>100 \mu\text{g kg}^{-1}$  in a variety of soil treated with ICD from France. Subsequently, accumulating neonicotinoids in agricultural soils have a high probability for transport to surface waters (Main et al., 2014).

The hydrologic transport of a compound to surface or groundwater systems is largely influenced by its sorption to soil. Reported ICD solid-to-solution partition coefficient ( $K_d$ ) values in a silt loam soil range from 1.4 to 14.4 L kg<sup>-1</sup> (Cox et al., 1997). Many studies agree that soil organic matter content (OM) or organic carbon content (OC) is the strongest predictor of ICD sorption values (Cox et al., 1998; Fernández-Pérez et al., 1998; Liu et al., 2006; Broznic et al., 2011). Soil texture and cation exchange capacity were also found to be significant predictors of ICD  $K_d$  values (Cox et al., 1997; Cox et al., 1998; Cox et al., 1998b; Liu et al., 2006; Broznic et al., 2011; Jeong et al., 2011). Liu et al. (2002) elucidated ICD sorption mechanisms by obtaining IR spectra after ICD sorption on Ca-saturated clay minerals and humic acid-clay complexes. The spectra suggested formation of hydrogen bonds between the N=N group of the imidazolidine ring and hydrated cations of clay minerals and hydroxyl groups of humic acids. In addition, the spectra suggested coordination bonds between the C=N group in pyridine ring and the exchangeable cation of clay and the formation of a hydrogen bond between the C=N group and a hydroxyl on the surface of humic acids. Several studies found pH to be an insignificant predictor of ICD sorption values (Cox et al., 1998b and Broznic et al., 2011).

With respect to previous research on ICD transport, few studies are found in the literature. Rômulo Penna et al. (2004), monitored ICD transport in a Dutch clay soil planted to winter wheat (*Triticum aestivum* L.) for one year and observed greater ICD concentration in the upper 10 cm of soil after 189 days. Not until day 328, after soil plowing, was ICD concentration greatest in the 10- to 20-cm layer. They attribute the downward movement of ICD to the mixing of the soil from plowing and concluded conducting individual column leaching experiments would better reveal ICD leaching characteristics. Fernández-Pérez et al. (1998) observed ICD transport in a layered soil column containing native soil, amended soil, peat and sand, and the

authors concluded that ICD has a low leaching potential in soil with high OM content. In comparison, Gupta et al. (2002) conducted a soil column ICD leaching experiment with a sand loam containing only 0.86% OM, and concluded that ICD has a greater potential to leach to groundwater in soil with low OM. The difference in OM content and ICD recovered in leachate between Fernández-Perez et al (1998) and Gupta et al. (2002) suggests that additional research is necessary to understand soil properties governing ICD leaching through soil.

Previous research has illustrated the ability of vegetation to reduce ICD mobility. Peterson (2007) observed greater extractable ICD concentration in vegetated columns compared to non-vegetated (control) columns over the course of a 2.5 year experiment. Differences between the columns were attributed a reduction of soil moisture in the vegetated soil columns; however, Peterson (2007) did not investigate plant uptake of ICD or vegetation influence on soil properties. The research indicating changes in ICD transport in the presence of vegetation presents an opportunity to evaluate land management techniques that may help mitigate ICD transport to water resources. Vegetative buffer strips (VBS), a row of vegetation, consisting of grasses, shrubs, trees or a combination of species, surrounding agricultural land or stream banks (Schultz et al., 1995), mitigate non-point source agrochemical pollutant transport (Lowrance et al., 1997) via physical, chemical and biological mechanisms. Vegetative buffer strips enhance runoff infiltration and trap sediment (Lin et al., 2011), increase agrochemical sorption (Chu et al., 2013b), and improve organic pollutant degradation (Mandelbaum et al., 1995; Lin et al., 2003; Lin et al., 2008). Soils within VBS typically contain greater OC content (Mandelbaum et al., 1995) and neonicotinoid sorption is generally enhanced in soils with greater OC content (Cox et al., 1998 and Rodriguez-Liebana et al., 2012). This suggests that VBS may alter the transport

of ICD and other neonicotinoids. Subsequently, VBS may help prevent untargeted organisms from ICD exposure and reduce the contamination of surface and drinking waters.

To date, no published studies have investigated neonicotinoid sorption and transport in VBS soils. Although some studies have investigated the fate and transport of ICD in soil, the basic reaction parameters, and influence of vegetative management (e.g. cropland, grass VBS or riparian VBS) on ICD transport in soil is still not fully understood. To date, no studies investigating ICD transport have employed chemical non-equilibrium transport models, such as HYRDUS-1D. The objectives of this research were to: (1) examine ICD sorption to soils from cropland, grass VBS and riparian VBS; (2) study ICD transport in the soils from the three vegetation treatments; and (3) fit ICD transport data to selected models to assess ICD sorption mechanisms and potential for transport in soil.

## **3.2 Materials and Methods**

### **3.2.1 Sampling sites, soil sampling, and soil characterization**

Sampling sites were chosen from public Conservation Areas (CA) managed by the Missouri Department of Conservation (MDC) that were located within the in the Central Claypan (113) and Iowa and Missouri Heavy Till Plain (109) Major Land Resource Areas of northern Missouri. After identification of potential sites meeting these criteria, ArcGIS software (ESRI ArcMap 10.02) was used to overlay a grid of cells (300 m x 300 m) over land use data (2011 National Land Cover Database, USGS) and aerial photography (2014 National Agriculture Imagery Program, USDA) associated with the sites. Each cell was evaluated to determine if it contained cropland, grassland, and riparian buffer. From over 100 cells each containing the three vegetation types, a total of six field sites (described in Table 3.1) were randomly selected for sampling.

**Table 3.1** Description of randomly selected sites containing adjacent cropland, grass buffer strips and riparian buffer strips.

| Site | Conservation Area             | Missouri County | Coordinates              | Soil   | Vegetation      |  |   |
|------|-------------------------------|-----------------|--------------------------|--|-----------------|--|---|
|      |                               |                 |                          |  | Crop            | Grass  | Riparian  |
| 1    | Bunch Hollow                  | Carroll         | 39.583512,<br>-93.593925 | Armster loam<br>(Mollic Hapludalfs)                                  | <i>Zea mays</i> | <i>Sorghastrum nutans</i> (L.)<br>Nash., <i>Andropogon gerardii</i><br>Vitman and <i>Sorghum</i><br><i>halpense</i>  | <i>Gleditisia triacanthos</i> L. and<br><i>Quercus velutina</i>   |
| 2    | Emmett and Leah Seat Memorial | Gentry          | 40.410882,<br>-94.239575 | Eroded Adair (Aquertic Argudolls) and Shelby (Typic Argudolls) loams | <i>Zea mays</i> | <i>Solidago</i> Genus, <i>Glyceria striata</i> (Lam.) Hitchc., <i>Sorghastrum nutans</i> (L.) Nash, and <i>Andropogon gerardii</i> Vitman.                 | <i>Acer saccharinum</i> L. and <i>Carya ovata</i>   |
| 3    | Thomas Hill Reservoir         | Macon           | 39.664385,<br>-92.594203 | Eroded Gifford silt loam (Vertic Epiqualfs)                          | <i>Zea mays</i> | <i>Schizachyrium scoparium</i> (Michx.) Nash., <i>Poa pratensis</i> , and <i>Glyceria striata</i> (Lam.) Hitchc.   | <i>Acer saccharinum</i> L. and <i>Carya ovata</i>   |
| 4    | Fountain Grove                | Livingston      | 39.737026,<br>-93.353689 | Chariton silt loam (Vertic Albaqualfs)                               | <i>Zea mays</i> | <i>Solidago</i> Genus, <i>Schizachyrium scoparium</i> (Michx.) Nash., <i>Glyceria striata</i> (Lam.) Hitchc., and <i>Bromus tectorum</i> L.                | <i>Fraxinus americana</i> L. and<br><i>Gleditisia triacanthos</i> L.  |
| 5    | Fountain Grove                | Livingston      | 39.723428,<br>-93.336124 | Chariton silt loam (Vertic Albaqualfs)                               | <i>Zea mays</i> | <i>Bromus tectorum</i> L., <i>Schizachyrium scoparium</i> (Michx.) Nash., <i>Glyceria striata</i> (Lam.) Hitchc., and <i>Sorghastrum nutans</i> (L.) Nash. | <i>Liriodendron tulipifera</i> L.,<br><i>Quercus palustris</i> Muench., and<br><i>Gleditisia triacanthos</i> L. |
| 6    | Locust Creek                  | Sullivan        | 40.171226,<br>-93.169927 | Frequently flooded Landes loam (Fluventic Hapludolls)                | <i>Zea mays</i> | <i>Bromus tectorum</i> L., <i>Glyceria striata</i> (Lam.) Hitchc., <i>Sorghastrum nutans</i> (L.) Nash., and <i>Andropogon gerardii</i> Vitman.            | <i>Quercus palustris</i> Muench., <i>Acer saccharinum</i> L., and<br><i>Gleditisia triacanthos</i> L.           |

At each of the six sites, soil (4 – 5 kg) was randomly collected at 0 – 10 cm depth at five locations within each vegetation type to create a composite sample for each site by vegetation combination (18 samples total). Within the forested riparian buffers, soil samples were collected at a distance of 30 – 50 cm from the base of the tree. Following collection, the samples were thoroughly mixed, air-dried, passed through a 2-mm sieve, and stored in plastic bags at room temperature. Soil samples were analyzed for the following list of parameters using methods (provided in parentheses) described in Burt (2004): particle size distribution (pipette); exchangeable bases (unbuffered  $\text{NH}_4\text{Cl}$ ) cation exchange capacity (CEC) (calculated by summation of cations exchanged in  $\text{NH}_4\text{Cl}$ ); total organic carbon and total nitrogen contents (Leco C/N analyzer; Leco Corp; St. Joseph, MI); and soil pH in water and salt (1:1 solid to solution ratio in water and 1:2 solid to solution ratio in 0.01 M  $\text{CaCl}_2$ ).

**Table 3.2** Mean soil characterization data and residual neonicotinoid concentrations for soils collected from six locations planted to riparian and grass buffer strips and cropland.

| Site | Location       | Land Management           | Soil Texture    | Clay % | Organic Carbon g kg <sup>-1</sup> | Total Nitrogen g kg <sup>-1</sup> | CEC <sup>a</sup> cmolc kg <sup>-1</sup> | pH <sub>w</sub> <sup>b</sup> | Neonicotinoid Summation <sup>c</sup> µg kg <sup>-1</sup> | Imidacloprid Summation µg kg <sup>-1</sup> |
|------|----------------|---------------------------|-----------------|--------|-----------------------------------|-----------------------------------|---|------------------------------|--|--|
| 1    | Bunch Hollow   | Crop<br>Grass<br>Riparian | Silt Loam       | 18.3   | 17.8                              | 1.67                              | 15.0                                    | 6.9                          | 19.21  | 13.81                                      |
|      |                |                           | Silt Loam       | 17.3   | 23.7                              | 1.86                              | 15.6                                    | 6.7                          | 0.30   | 0  |
|      |                |                           | Loam            | 17.5   | 28.8                              | 2.47                              | 17.0                                    | 6.7                          | 0.23   | 0  |
| 2    | Seat Memorial  | Crop<br>Grass<br>Riparian | Loam            | 24.9   | 24.4                              | 2.25                              | 17.6                                    | 6.5                          | 8.10   | 0  |
|      |                |                           | Loam            | 24.9   | 32.7                              | 2.92                              | 20.0                                    | 6.7                          | 0.51   | 0  |
|      |                |                           | Loam            | 21.8   | 39.8                              | 3.21                              | 23.2                                    | 6.2                          | 0.19   | 0  |
| 3    | Thomas Hill    | Crop<br>Grass<br>Riparian | Silt Loam       | 17.2   | 12.5                              | 1.28                              | 11.3                                    | 6.2                          | 0.80   | 0  |
|      |                |                           | Silt Loam       | 19.6   | 30.6                              | 2.75                              | 15.0                                    | 6.3                          | 0  | 0  |
|      |                |                           | Silt Loam       | 17.4   | 36.9                              | 3.23                              | 19.1                                    | 7.2                          | 0.22   | 0  |
| 4    | Forest Grove 1 | Crop<br>Grass<br>Riparian | Silt Loam       | 21.3   | 23.1                              | 2.08                              | 19.4                                    | 5.6                          | 12.82  | 3.37                                       |
|      |                |                           | Silty Clay Loam | 30.3   | 40.7                              | 3.68                              | 26.2                                    | 5.9                          | 1.06   | 0  |
|      |                |                           | Silt Loam       | 25.0   | 58.5                              | 4.70                              | 30.4                                    | 5.8                          | 0.89   | 0  |
| 5    | Forest Grove 2 | Crop<br>Grass<br>Riparian | Silt Loam       | 25.2   | 26.6                              | 2.61                              | 22.3                                    | 5.7                          | 19.95  | 4.47                                       |
|      |                |                           | Silt Loam       | 26.0   | 37.0                              | 3.31                              | 25.1                                    | 5.9                          | 0.80   | 0.31                                       |
|      |                |                           | Silt Loam       | 23.7   | 45.4                              | 4.41                              | 31.2                                    | 6.4                          | 0.43   | 0  |
| 6    | Locust Creek   | Crop<br>Grass<br>Riparian | Silt Loam       | 17.1   | 15.4                              | 1.40                              | 15.2                                    | 5.7                          | 14.65  | 0  |
|      |                |                           | Silt Loam       | 18.7   | 17.4                              | 1.62                              | 14.0                                    | 5.5                          | 0  | 0  |
|      |                |                           | Loam            | 16.5   | 23.2                              | 2.01                              | 17.9                                    | 5.9                          | 0  | 0  |

<sup>a</sup> CEC, cation exchange capacity

<sup>b</sup> pH water

<sup>c</sup> Neonicotinoid Summation: summation of residual imidacloprid, acetamiprid, clothianidin, dimethoate, dinotefuran, metalaxyl, thiacloprid, and thiamethoxam extracted from each sample

### 3.2.2. Residual Neonicotinoid Concentrations

Residual soil ICD, acetamiprid, clothianidin, dimethoate, dinotefuran, metalaxyl, thiacloprid, and thiamethoxam were measured at the University of Nebraska Water Sciences Laboratory (Lincoln, Nebraska) using microwave assisted solvent extraction followed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) (Snow D., personal communication, 2016). The method was validated according to standard protocols for analysis of environmental contaminants (USEPA, 1986) and extraction/instrumental conditions are similar to previously published methods (Coscollà et al., 2009; Snow et al., 2013). High purity methanol and other reagents were purchased from Fisher Scientific (Saint Louis, MO), while reference neonicotinoid compounds were obtained from Sigma Aldrich (St. Louis, MO). Isotopically labeled internal standards (d3-Clothianidin, d4-Imidacloprid, d3-thiamethoxam and d6-metalaxyl) were obtained from Sigma Aldrich. Stock solutions (5.0 µg/µL) of all compounds were prepared by dissolving a suitable amount in methanol. Spiking (5.0 ng/µL) and calibration (0.0000, 0.0001, 0.0006, 0.0125, 0.0375, 0.0625 and 0.1250 ng/µL) solutions were prepared by dilution of mixed and diluted stock solutions in methanol.

Neonicotinoid were extracted from 2-3 gram soil samples weighed into a 20 mL volume Teflon microwave digestion vessel (MARS XPress, CEM Corporation, Matthews NC). A separate portion of each sample was analyzed for gravimetric moisture content. Butylated hydroxytoluene (1.0 mg) was mixed with the sample to minimize potential effects from oxidation during extraction. Surrogate compounds (50 ng each nitenpyram and terbuthyazine) were added and mixed with sample along with 8 mL of a 1:1 mixture of methanol and acetonitrile containing 0.01% ammonium hydroxide. Samples and quality control mixtures were heated using a power of 400 watts to a temperature of 90°C for 10 minutes, and then allowed to

cool to room temperature. The entire mixture was then transferred to 50 mL polypropylene centrifuge tubes, and extraction vessel rinsed with 8 mL of methanol to quantitatively transfer contents. Extract was centrifuged for 10 minutes at 3000 rpm and supernatant transferred to evaporation tube (Labconco RapidVap N2, Kansas City, MO). The contents of the centrifuge tube were mixed with an additional 8 mL of methanol, centrifuged a second time and the supernate combined. Extracts were then spiked with internal standards (50 ng of labelled compounds) and evaporated under nitrogen at 40°C. Residue was dissolved in 400 µL of a 20% mixture of methanol in water and transferred to a silane-treated insert in a 2 mL autosampler vial.

A Waters 2695 high pressure liquid chromatograph (HPLC) interfaced with a Quattro Micro triple quadrupole mass

**Table 3.3** Source conditions used for LC-MS/MS.

| Parameter              | Value |
|------------------------|-------|
| Corona current (µA)    | 3.0   |
| Extractor voltage (V)  | 4.0   |
| RF Lens voltage (V)    | 0.2   |
| Source Temp. (°C)      | 150   |
| APCI Probe Temp. (°C)  | 425   |
| Desolvation gas (L/hr) | 600   |
| Cone gas (L/hr)        | 50    |

spectrometer was used for separation and quantification of the neonicotinoid insecticides by LC-MS/MS. An end-capped BetaBasic C18 (Thermo Scientific, San Jose, CA) reverse phase column (250x2 mm) using a gradient separation was used for the chromatographic separation. Mobile phases were 0.15% formic acid in methanol/water (97:3) followed by 0.15% formic acid in water/methanol (97:3); at a constant temperature of 50°C and a flow rate of 0.3 mL/min. Analysis run time is designed for 30 minutes. Positive ion mode atmospheric pressure chemical ionization (APCI). Tandem mass spectrometry multiple reaction monitoring was used for identification and quantitation. A pseudo-molecular ion  $[M+H]^+$  is selected as the parent ion for fragmentation, and corresponding fragment ion(s) is selected for identification and quantitation.

Ionization and collision energies are optimized based on procedures described by the instrument manufacturer (Tables 3.3 and 3.4).

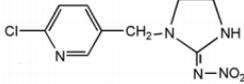
**Table 3.4** Compounds measured with multiple reaction monitoring (MRM) parameters, cone voltage and collision energies (dwell = 0.2 sec).

| Analyte                              | Parent Ion (m/z) | Fragment Ion (m/z) | Cone Voltage (kV) | Collision Energy |
|--------------------------------------|------------------|--------------------|-------------------|------------------|
| Acetamiprid                          | 223.1            | 126.1              | 27                | 18               |
| Clothianidin                         | 250.1            | 169.0              | 19                | 18               |
| Dinotefuran                          | 203.0            | 129.0              | 12                | 12               |
| Imidacloprid                         | 256.0            | 209.3              | 27                | 18               |
| Nitenpyram                           | 271.0            | 126.0              | 15                | 27               |
| Thiacloprid                          | 253.0            | 126.0              | 28                | 22               |
| Thiamethoxam                         | 292.1            | 211.0              | 27                | 18               |
| <b>Internal Standards/Surrogates</b> |                  |                    |                   |                  |
| d <sub>3</sub> -Clothianidin (IS)    | 253.1            | 172.0              | 19                | 18               |
| d <sub>4</sub> -Imidacloprid (IS)    | 260.0            | 213.1              | 27                | 18               |
| d <sub>3</sub> -Thiamethoxam (IS)    | 295.1            | 214.0              | 27                | 18               |
| d <sub>6</sub> -Metalaxyl (IS)       | 286.1            | 226.2              | 20                | 13               |
| Terbutylazine                        | 230.0            | 174.0              | 33                | 17               |

### 3.2.4 Sorption Experiment

<sup>14</sup>C-labeled ICD [pyridyl 2,6-<sup>14</sup>C] (0.222 mCi mg ICD<sup>-1</sup>) was purchased from Institute of Isotopes Co. (Budapest, Hungary). Chemical properties are displayed in Table 3.5.

**Table 3.5** Selected chemical properties of imidacloprid<sup>a</sup>.

| Chemical Structure  | Molecular Weight    | S <sub>w</sub> <sup>b</sup> | GUS Index Value <sup>c</sup><br>(Leaching Potential) | Log K <sub>ow</sub> <sup>d</sup> | pK <sub>a</sub> <sup>e</sup> |
|---|---------------------|-----------------------------|--|----------------------------------|------------------------------|
|   | g mol <sup>-1</sup> | mM                          |  |                                  |                              |
|  | 255.7               | 2.01                        | 3.76 (High)  | 0.57                             | 1.56, 11.1                   |

<sup>a</sup>Data were obtained from PPDB (2014) and Fossen (2006).

<sup>b</sup>S<sub>w</sub>, water solubility.

<sup>c</sup>GUS, Groundwater Ubiquity Score, and associated Leaching Potential classification.

<sup>d</sup>K<sub>ow</sub>, octanol-water partition coefficient.

<sup>e</sup>pK<sub>a</sub>, acid dissociation constants, Chamberlain et al., (1996).

Seven grams of air-dried soil was placed in 50-mL polypropylene copolymer centrifuge tubes and suspended in 35 mL CaCl<sub>2</sub> (I=0.01 mol L<sup>-1</sup>) background electrolyte solution to achieve a 1:5 (w/v) soil to solution ratio. The initial aqueous phase

concentration of  $^{14}\text{C}$ -ICD (pyridyl 2,6- $^{14}\text{C}$ ; Institute of Isotopes Co., Budapest, Hungary) was  $100\ \mu\text{g kg}^{-1}$  soil, and this concentration was based on measured field soil concentrations ranging from  $<0.1\ \mu\text{g kg}^{-1}$  to  $>100\ \mu\text{g kg}^{-1}$  (Bonmatin et al., 2005). To insure detection, the high end of observed ICD field concentrations was evaluated in this study. To inhibit microbial degradation,  $\text{NaN}_3$  was added to achieve a final a concentration of  $0.0015\ \text{M}$  or  $1.5\ \text{mM}$  (Wolf et al., 1989). After addition of solution, tubes were wrapped in aluminum foil and agitated on end-over-end shakers (7 rpm) at  $25^\circ\text{C}$  for 22 h. Preliminary experiments indicated that sorption equilibrium was achieved within 20 h. Samples, controls ( $0\ \mu\text{M}$  ICD), and adsorbent-free controls (no soil) were reacted in triplicate. After reaction, tubes were centrifuged at 13,000 rpm for 15 min. The supernatant solution was filtered through a  $0.45\text{-}\mu\text{m}$  nominal pore size polytetrafluoroethylene membrane filter, and 1 mL of solution was added to 4 mL of UltimaGold liquid Scintillation Cocktail (PerkinElmer UltimaGold™ AB, Waltham, MA). Samples were read for 10 min and 2% error on a Beckman LC 6000SC liquid scintillation counter (Fullerton, CA). A calibration curve was created for LSC method from spiking  $\text{CaCl}_2/\text{NaN}_3$  solution with known  $^{14}\text{C}$  ICD concentrations ranging from  $0\ \mu\text{g L}^{-1}$  to  $17\ \mu\text{g L}^{-1}$ .

### 3.2.4.1 Mathematical description

The amount of ICD adsorbed to soil after reaction was calculated using Eq. 1.

$$q_{ads} = \frac{(C_{ads,B})(V_B) - (C_{ads,S})(V_S)}{m_s} \quad [1]$$

where  $q_{ads}$  is the surface excess of ICD (i.e., amount adsorbed) after the reaction period ( $\mu\text{mol kg}^{-1}$ ),  $C_{ads,B}$  and  $C_{ads,S}$  are the equilibrium ICD concentrations ( $\mu\text{mol L}^{-1}$ ) in blank (B) and samples (S) after reaction,  $V_B$  and  $V_S$  are the volume of solution (L) added to

samples and blanks, and  $m_s$  is mass of soil (kg) added to the reaction vessel (Essington, 2004). The solid-to-solution partition coefficient ( $K_d$ ) was calculated by dividing  $q_{ads}$  by  $C_{ads,S}$ .

#### **3.2.4.2 Statistical Analyses**

Analysis of variance with Duncan's multiple range test was used to analyze the data using SAS (SAS Inst., 2015) assuming a randomized complete block design with six blocks (sites) and three vegetative treatments (crop, grass and riparian). Statistical differences were tested at  $\alpha = 0.05$ . Prediction equations for  $\log K_d$  of ICD as a function of soil properties and initial ICD concentration were estimated using stepwise multiple regression analysis.

#### **3.2.5 Leaching Experiment**

Soil from Thomas Hill Reservoir was chosen for the leaching experiment due to noticeable differences in  $K_d$  values between soil treatments. Soil from Forest Grove 1, exhibiting the greatest differences in  $K_d$  values, was not chosen due to high  $K_d$  values that could have resulted in leaching experiments requiring unreasonably lengthy periods of time to complete. Glass columns were custom made of durable glass with polyethylene end caps and fittings (Kimble Chase, Vineland, NJ). Column inner diameter and length were 7.5 cm and 15 cm, respectively. A layer of nylon Nitex® mesh (10  $\mu\text{m}$  aperture) was placed on the bottom end caps of each column to retain solid materials within the columns. Heat treated glass beads (0.8-1.2 mm), baked at 400°F for 24 h, were packed about 3 cm thick on the nylon mesh covering the outlet to occupy the slightly tapered end of the column. On top of the glass beads, a 0.5 cm layer of heat treated fine quartz sand, baked at 400°F for 24 h, was added and smoothed to provide a flat surface. Air-dried soil

passed through a 1 mm mesh size-opening sieve was packed to a height of 10.5 cm and a bulk density of  $1.1 \text{ g cm}^{-3}$ . Glass beads with a layer thickness of 3 cm were placed on top of the soil column to more evenly distribute water and prevent splash erosion and surface sealing. Columns were prepared in duplicate for each vegetative management.

### **3.2.5.1 Bromide tracer**

Each soil column was gradually saturated with  $\text{CaCl}_2$  solution ( $I = 0.01 \text{ mol L}^{-1}$ ) containing  $0.0015 \text{ M NaN}_3$  from below over a 48 h time period. After saturation of the column, a Masterflex L/S pump (Vernon Hills, IL) was used to add solution to the top of the column and a fraction collector (Teledyne Isco Foxy 200, Lincoln, NE) was used to collect the outflow from the bottom of the column. The soil column was irrigated with  $0.01 \text{ M}$  ionic strength  $\text{CaCl}_2$  containing  $0.0015 \text{ M NaN}_3$  at a rate of  $0.25 \text{ cm h}^{-1}$  to establish a steady flow. No vacuum was applied at the bottom of the column. The outflow rate was confirmed via monitoring of leachate fraction volumes. When constant water flow was established, a 2-h pulse of bromide tracer ( $8.4 \text{ mM KBr}$ ) was applied and eluted with  $\text{CaCl}_2$  solution. The leachate was collected every 0.5 h into polypropylene copolymer tubes for a total of 144 h. The tubes were capped three times a day to prevent evaporation loss. Bromide concentrations were normalized to the initial concentration ( $C_0$ ), and  $\text{Br}^-$  breakthrough curves (BTC) were determined for each repacked column to describe water flow behavior prior to ICD addition to estimate physical equilibrium transport parameters.

### **3.2.5.2 Imidacloprid Transport**

Radio-labeled ( $^{14}\text{C}$ ) ICD was diluted in  $\text{CaCl}_2$  ( $I = 0.01 \text{ M}$ ) solution containing  $0.0015 \text{ M NaN}_3$  solution to achieve an ICD concentration of  $100 \text{ } \mu\text{g ICD kg}^{-1}$  soil. The

ICD solution was applied at the same flow rate as the Br<sup>-</sup> tracer and pulsed into the columns for 10 h. The crop, grass VBS, and riparian VBS columns were continuously irrigated with CaCl<sub>2</sub> solution for 700 h (26.2 pore volumes) and 1,100 h (41.2 pore volumes), respectively, at the same steady flow rate. Leachate fraction was collected every 0.5 h in polypropylene co-polymer tubes and capped every 8 h to prevent evaporative loss.

The concentration of Br<sup>-</sup> in each fraction was determined with a Dionex ICS-1000 ion chromatography (IC) unit (Dionex Corp.; Sunnyvale, CA) equipped with a IonPac® AS14A (4 x 250 mm) anion column, and AS40 autosampler. Solution eluent (Dionex™ AS14A Eluent Concentrate) was pumped at a flow rate of 1.0 mL min<sup>-1</sup> and standards (Dionex™ Combined Seven Anion Standard II) ranging from 0 to 500 μM Br<sup>-</sup> were used to create a standard curve.

Liquid scintillation counting was used to determine the concentration of <sup>14</sup>C-ICD in leachate. One milliliter of solution from each column leachate sample was added to a 7 mL scintillation vial containing 4 mL of scintillation cocktail (PerkinElmer UltimaGold™ AB, Waltham, MA). Samples were analyzed for radioactivity using a Beckman LS 6000SC liquid scintillation counter (Fullerton, CA). Leachate pH and determination of ICD degradates was measured in every 50<sup>th</sup> sample. Degradation was measured using a high-performance liquid chromatography unit (Shimadzu, Columbia, MD) with a flow scintillation analyzer. A Zorbax Eclipse XDB C<sub>18</sub> column (2.1 mm x 200 mm; 3.5 μm; Agilent Technologies, Santa Clara, CA) was used. The mobile phase for HPLC consisted of 100% acetonitrile and 5 mM formic acid in water (solvents A and B, respectively) with a flow rate of 1.2 mL min<sup>-1</sup>. The gradient method was as follows (%A:%B): 98:2 from 0-

1 min; ramp to 95:5 from 1 to 3 min; 95:5 held from 3-4 min; ramp to 2:98 from 4 to 5.5 min; 2:98 held from 5.5 to 6.5 min. Calibration standards (0 to 0.09  $\mu\text{Ci mL}^{-1}$ ) were prepared by dilution of ICD stock solutions in Millipore water. The detection limit was determined to be 0.003  $\mu\text{Ci mL}^{-1}$ . Retention time for ICD and degradates were 2.37 min (desnitro-imidacloprid hydrochloride), 2.45 min (6-chloropyridine-3-carboxylic acid) and 2.56 min (ICD). Lack of peaks associated with ICD degradation products was interpreted as absence of ICD degradation within the columns due to constant addition of  $\text{NaN}_3$ .

### 3.2.5.3 Parameter estimation

Transport parameters were estimated by solving the inverse problem using the non-linear least-squares optimization. The computer program CXTFIT (Toride et al., 1995) was used to analyze bromide BTCs and estimate the physical transport parameters for each column. Then using physical transport estimated parameters for  $\text{Br}^-$ , the computer program HYDRUS-1D (Simunek et al., 2009) was used to determine the chemical transport processes for ICD in each column. Numerous iterations were performed to determine the best fit model.

More complex three-site sorption models have been used to describe sulfonamide antibiotic transport in repacked soil columns (Wehrhan et al. 2007; Chu et al., 2013). The model assumes the sorbate concentration ( $S$ ) is the sum of the solute concentration ( $M_{\text{solute}}M_{\text{total soil}}^{-1}$ ) on (i) instantaneous sorption sites ( $S_1$ ), (ii) kinetic sorption sites ( $S_2$ ) and irreversible sorption sites ( $S_3$ ):

$$S = S_1 + S_2 + S_3 \quad [2]$$

Instantaneous sorption sites follow a linear relationship with the liquid phase solute concentration in Eq. [3]. Kinetic sorption sites ( $S_2$ ) follow a first-order kinetic sorption

rate in Eq. [4] Irreversible sorption sites follow a first-order kinetic sink for liquid phase solutes in Eq. [5].

$$S_1 = f K_d C \quad [3]$$

$$\frac{dS_2}{dt} = \alpha_2 [(1 - f)K_d C - S_2] \quad [4]$$

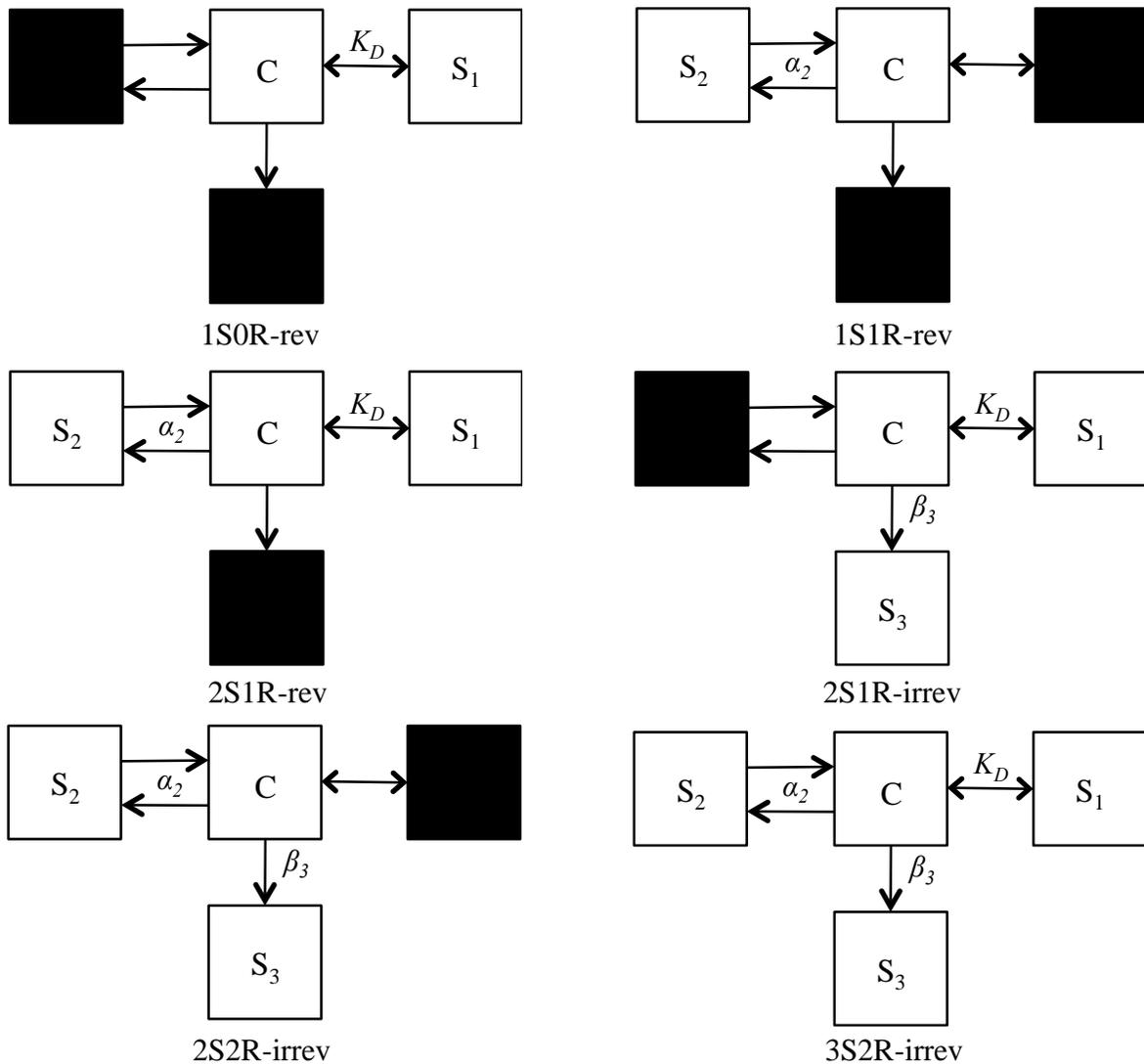
$$\frac{\partial S_3}{\partial t} = \frac{\theta}{\rho} \beta_3 C \quad [5]$$

where  $f$  is the fraction of Type 1 sorption sites available for instantaneous sorption;  $C$  is the solute concentration, ( $M L^{-3}$ ;  $M$ , unit of mass;  $L$ , unit of length,  $t$  is time (T);  $\alpha_2$  is the first-order sorption kinetic rate constant at the second adsorption site ( $T^{-1}$ );  $\theta$  is the volumetric water content ( $L^3 L^{-3}$ ), which is equal to porosity for saturated experiments;  $\rho$  is the bulk density ( $M L^{-3}$ );  $\beta_3$  is the irreversible adsorption rate ( $T^{-1}$ ); and  $K_d$  has been described previously.

A three-site, two-rate irreversible model (3S2R-irrev) is created by combining Eq. [3], [4] and [5] as shown in Eq. [6]. Omitting different sites permits the development of a variety of sorption models (Fig. 3.1).

$$\theta \frac{\partial C}{\partial t} + \rho f K_d C + \rho \alpha_2 [(1 - f)K_d C - S_2] + \theta \beta_3 C = \theta D \frac{\partial^2 C}{\partial z^2} - q \frac{\partial C}{\partial z} \quad [6]$$

where  $z$  is the depth and all other variables have been previously described (Jury and Horton, 2004).



**Figure 3.1** Linear sorption models fitted using HYDRUS 1D. The model names represent the number of sites (S), number of rates (R), and reversibility of sorbate removal from a site (rev: reversible, irrev: irreversible).  $C$  is the liquid phase with solute concentration  $C$ ,  $S_1$  is an instantaneous sorption site,  $S_2$  is a kinetic sorption site and  $S_3$  is irreversible sorption site.  $K_d$  is the solid to solution distribution coefficient,  $\alpha_2$  is the reversible adsorption/desorption rate and  $\beta_3$  is the irreversible adsorption rate. Black boxes represent omission of sorption sites. Developed after Wehrhan et al. (2007).

For all estimations, the flux density ( $q$ ) was determined experimentally, and the soil water content ( $\theta$ ) was assumed to be the saturation water content. In the case of  $\text{Br}^-$  modeling, the estimated transport parameters from CXTFIT were dispersion coefficient ( $D$ ) and pore water velocity ( $v$ ), and dispersivity ( $\lambda$ ) was calculated using  $\lambda=D/v$ . For ICD modeling, the estimated transport parameters include: the  $K_d$ ; the reversible adsorption/desorption rate ( $\alpha_2$ ) for sorption on the kinetic sorption sites ( $S_2$ ); the fraction of instantaneous sorption sites ( $f$ ), and the irreversible adsorption rate ( $\beta_3$ ). The goodness of the model fit was measured by the value of the model efficiency (EF), and model efficiency was calculated using Equation [7]:

$$EF = \frac{\Sigma(O_i - O_{mean})^2 - \Sigma(O_i - P_i)^2}{\Sigma(O_i - O_{mean})} \quad [7]$$

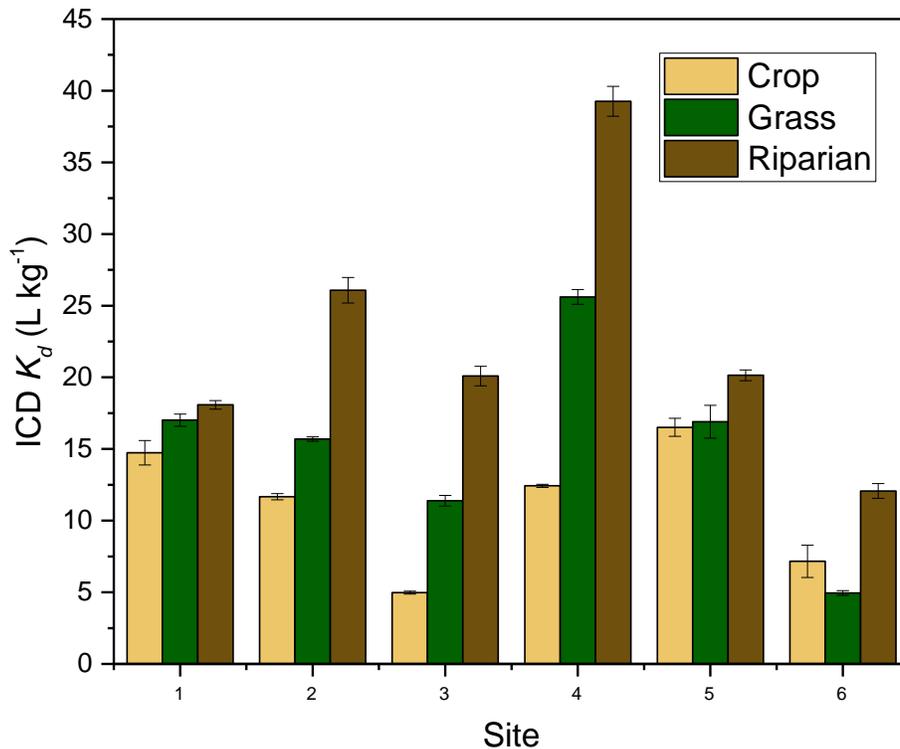
where  $O_i$  and  $P_i$  are the observed and predicted values, respectively, and  $O_{mean}$  is the arithmetic mean of the observed values (Blevins et al., 1978). The greater the EF value, the better the model fits the BTCs.

### 3.3 Results and Discussion

#### 3.3.1 Solid-solution partition coefficients ( $K_d$ )

Sorption of ICD was moderate to strong for all soil treatments, ranging from 5 to 40 L kg<sup>-1</sup> and an overall mean of 17.4 L kg<sup>-1</sup> (Figure 3.2). Analysis of variance results show that a significant ( $\alpha = 0.05$ ) main factor effect was observed for vegetative management ( $p = 0.044$ ) on  $K_d$  values, but not location ( $p = 0.079$ ). Figure 3.2 shows ICD  $K_d$  values by vegetative management and site. Mean  $K_d$  values for ICD adsorption were 11.2, 18.2, and 22.6 L kg<sup>-1</sup> for crop, grass VBS and riparian VBS soil, respectively. This agrees with ICD  $K_d$  values found in the literature (Cox et al., 1997). Duncan's multiple

range test results demonstrated that ICD  $K_d$  values for riparian VBS soils were significantly greater ( $p < 0.05$ ) than ICD  $K_d$  values associated with cropland soils, and ICD  $K_d$  values for grass VBS soil were intermediate and did not significantly differ from  $K_d$  values for cropland or riparian VBS soils ( $p = 0.312$  and  $0.859$ , respectively).



**Figure 3.2** Mean imidacloprid solid-solution partition coefficients ( $K_d$ ) for cropland, grass vegetative buffers, and riparian vegetative buffer soils collected at six sites in northern Missouri. Error bars represent one standard deviation.

Cumulatively, the  $K_d$  data indicated that soils under riparian VBS management exhibit enhanced ICD sorption relative to cropland management at environmentally relevant concentrations. This suggests that the sorptive capabilities of riparian VBS soils may help reduce the loss of neonicotinoids from agroecosystems. In agreement with our

study, Fernandez-Perez et al. (1998) reported increased ICD soil sorption in land management systems contributing more soil carbon (peat and native vegetation) compared to little to no carbon (amended soil and no vegetation). To the best of our knowledge, this is the first report indicating the potential of VBS treatments to sorb ICD to a greater extent than cropland treatment. Therefore, riparian vegetation provides ecosystem services, such as ICD retention and mitigation.

### **3.3.2 Correlation of sorption to soil properties**

Linear correlation coefficients for ICD  $K_d$  values with soil properties are listed in Table 3.6. The  $K_d$  values exhibit the strongest and most significant correlation with organic carbon (OC) content and weaker correlations with total nitrogen (N), cation exchange capacity (CEC), clay content and  $\text{pH}_{\text{water}}$ . Thus, OC alone explains 81.93% of the variance (Figure 3.2). To further model the relationships between ICD  $K_d$  values and soil properties stepwise multiple regression analysis was used. The inclusion of additional parameters ( $\text{pH}_{\text{water}}$  and CEC) in the model (Figure 3.3) resulted in slightly greater explanation of variance.

Organic carbon has been reported by others as a strong predictor of ICD adsorption (Cox et al., 1998; Koskinen et al., 2000; Broznic et al., 2012). When little to no organic carbon was present in soil, CEC and soil texture were noted as good predictors of  $K_d$  values of ICD (Fernandez-Bayo et al., 2008). In a study of ICD adsorption to six soils, Broznic et al. (2012) and Liu et al. (2006) also observed organic carbon to explain the greatest variance when a multiple regression analysis was performed. In addition, Liu et al. (2006) observed soil organic matter (SOM) to explain the greatest variance in a study of ICD adsorption each to six soils when a multiple regression analysis was

performed. However, the models developed by Liu et al. (2006) and Broznic et al. (2012) included clay content, which was not found to be as useful our predictive model.

A positive correlation of pH and ICD  $K_d$  values in the multi-parameter model agrees with previous research (Liu et al., 2006). However, only 2.23% of additional variance can be explained by adding  $\text{pH}_{\text{water}}$  to the model containing OC. This finding is likely due to  $\text{pH}_{\text{water}}$  values in the examined soils ranging only from pH 5.0 to 7.2. Additionally, Farenhorst (2006) postulated that soil pH impacts pesticide sorption when it is within two units of the  $pK_a$  and this range of pH values is well below the  $pK_a$  value of ICD ( $pK_a = 11.2$ ).

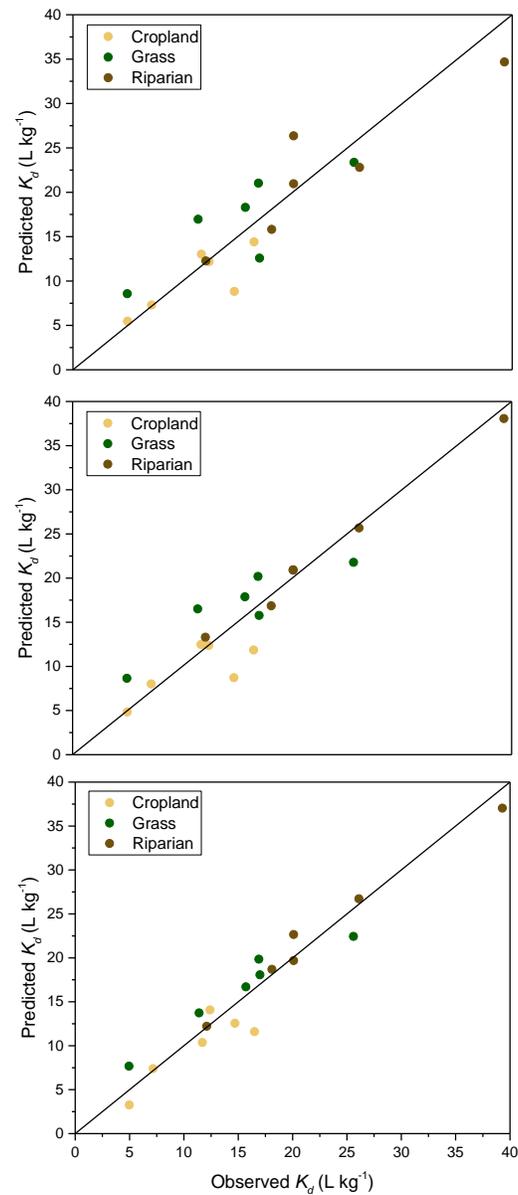
Inclusion of CEC in the stepwise multiple linear regression model explained an additional 1.20% of the variance over the model including OC and  $\text{pH}_{\text{salt}}$ . A positive correlation of CEC and ICD  $K_d$  values is in agreement with previous research (Liu et al., 2006 and Bronzic et al., 2012).

Total N is the second strongest predictor, but is not included in the stepwise multiple linear regression due to collinearity with OC. We postulate that total nitrogen content may indicate the importance of a different pool of soil organic matter or soil organic matter chemical characteristics. For example, Bailey et al. (2009) observed greater concentrations of particulate organic matter nitrogen (POM-N) and water extractable organic nitrogen (WEON) in upland tree-grass and grass VBS relative to cropland soil. In the same system, Veum et al. (2012) found differences in particulate, adsorbed and occluded (PAO) carbon and nitrogen between the treatments. The VBS soils contained greater PAO-C and PAO-N, and data suggest reduced SOC decomposition within the physically stable soil fraction (PAO).

There are no published studies investigating alteration of SOM chemical structure at any of the six sites studied. However, land management practices have been observed to influence SOM chemical structure via spectroscopic studies (Condrón and Newman, 1998; De Alcantara et al, 2004; Veum et al., 2014). We postulate that changes in SOM fractions and chemical composition within VBS may play a significant role in ICD sorption to the soils studied.

**Table 3.6** Linear correlation coefficients between imidacloprid solid to solution partition coefficients ( $K_d$ ) and soil properties.

| Statistic | Soil Properties |                |                          |              |                     |
|-----------|-----------------|----------------|--------------------------|--------------|---------------------|
|           | Organic Carbon  | Total Nitrogen | Cation Exchange Capacity | Clay Content | pH <sub>water</sub> |
| R         | 0.90517         | 0.84224        | 0.79423                  | 0.50445      | 0.43875             |
| p value   | <0.0001         | <0.0001        | <0.0001                  | 0.0328       | 0.0685              |



**Figure 3.3** Plot of predicted versus observed solid to solution distribution coefficient ( $K_d$ ) using multiple regression model and experimental  $K_d$ . Predicted values were determined using the following regression models (a)  $K_d = -20.7 + 0.754$  (Organic Carbon),  $r^2 = 0.819$ ; (b)  $K_d = -20.7 + 0.754$  (Organic Carbon) +  $3.63$  ( $\text{pH}_{\text{water}}$ ),  $r^2 = 0.842$ ; (c)  $K_d = 20.7 + 0.754$  (Organic Carbon) +  $3.63$  ( $\text{pH}_{\text{water}}$ ), -  $0.399$  (CEC),  $r^2 = 0.854$ .

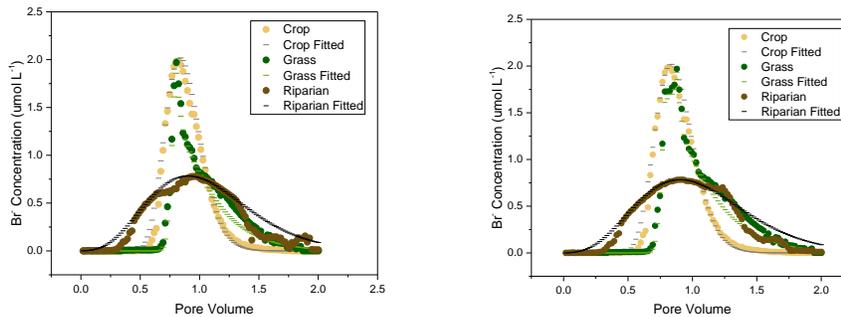
### 3.3.3 Bromide Transport

The BTCs of the conservative, anionic  $\text{Br}^-$  tracer describe water movement in each column containing soil from Forest Grove Reservoir, allowing us to distinguish the

effects of chemical nonequilibrium from physical nonequilibrium when comparing  $\text{Br}^-$  and ICD BTCs. The measured  $\text{Br}^-$  BTCs and model fits are shown in Figure 3.4. The measured peak pore volume for each vegetative management occurs slightly before one pore volume, indicating physical equilibrium. The soil columns were repacked with 1-mm sieved soil; therefore, they should not contain macropores that cause preferential flow. All the BTCs display tailing for the falling limb of the curve, the riparian and grass VBS being the most notable. In addition, peak  $\text{Br}^-$  concentration of the riparian soil BTC is significantly less than the cropland and grass soil BTCs. We speculate the tailing and reduced peak concentration is due to soil structure disparities, anion adsorption and mineralogical differences in the riparian zone rather than physical nonequilibrium. Although soil was sieved to 1-mm, riparian soil particles remained aggregated, whereas, crop and grass VBS soil were less aggregated. To our knowledge no studies exist investigating bromide transport in microaggregates ( $< 3 \text{ mm}$ ). However, Nielsen and Biggar (1962) found increasing aggregate size resulted in early appearance of the tracer from miscible displacement experiments, indicating the effect of preferential flow. In addition, intra-aggregate pore distribution consists of finer and more tortuous pores increasing the chemical flow path (Horn et al., 1994). Therefore, the chemical exchange process is retarded. In turn, we postulate microaggregation in the riparian VBS soil results in earlier detection of  $\text{Br}^-$  and creates a more tortuous path favoring a more disperse BTC.

The total N of the cropland, grass VBS, and riparian VBS soil was 1.28, 2.75 and 3.23  $\text{g kg soil}^{-1}$ , respectively, potentially resulting in a greater number of protonated nitrogen functional groups in the riparian VBS soil. Therefore, the greater number of

protonated sites in the riparian soil could facilitate anion adsorption. Chu et al. (2012) also found a reduced peak concentration in riparian soil packed to equilibrium in the same experimental setup. They speculated this occurred due to increased positive charge on the surface of aluminum and iron oxides as well as a proportion of kaolinite in the riparian soil compared to the cropland soil. We speculate that soil aggregation and increased  $\text{Br}^-$  sorption is the cause of the asymmetrical shape of  $\text{Br}^-$  BTCs. Therefore, a physical equilibrium CDE was used to describe the  $\text{Br}^-$  BTCs and the transport parameters  $D$  and  $v$  were fit using CXTFIT (Table 3.7).



**Figure 3.4** Bromide breakthrough curves for the cropland, grass VBS, riparian VBS columns and simulated fits obtained using a physical equilibrium model and the CXTFIT software.

**Table 3.7** Estimated parameters and experimental conditions for saturated soil column experiments (95% confidence intervals are shown in parentheses).

| Column       | $q^a$ | $\rho^b$ | $v^c$         | $\theta^d$ | $D^e$        |
|--------------|-------|----------|---------------|------------|--------------|
| Cropland     | 0.23  | 1.1      | 0.566 (0.001) | 0.51       | 0.14 (0.003) |
| Grass VBS    | 0.23  | 1.1      | 0.512 (0.02)  | 0.47       | 0.12 (0.03)  |
| Riparian VBS | 0.23  | 1.1      | 0.615 (0.05)  | 0.56       | 0.2 (0.04)   |

<sup>a</sup>  $q$ , ( $\text{cm h}^{-1}$ ) the flow rate; measured experimentally.

<sup>b</sup>  $\rho$ , ( $\text{g cm}^{-3}$ ) soil bulk density; measured.

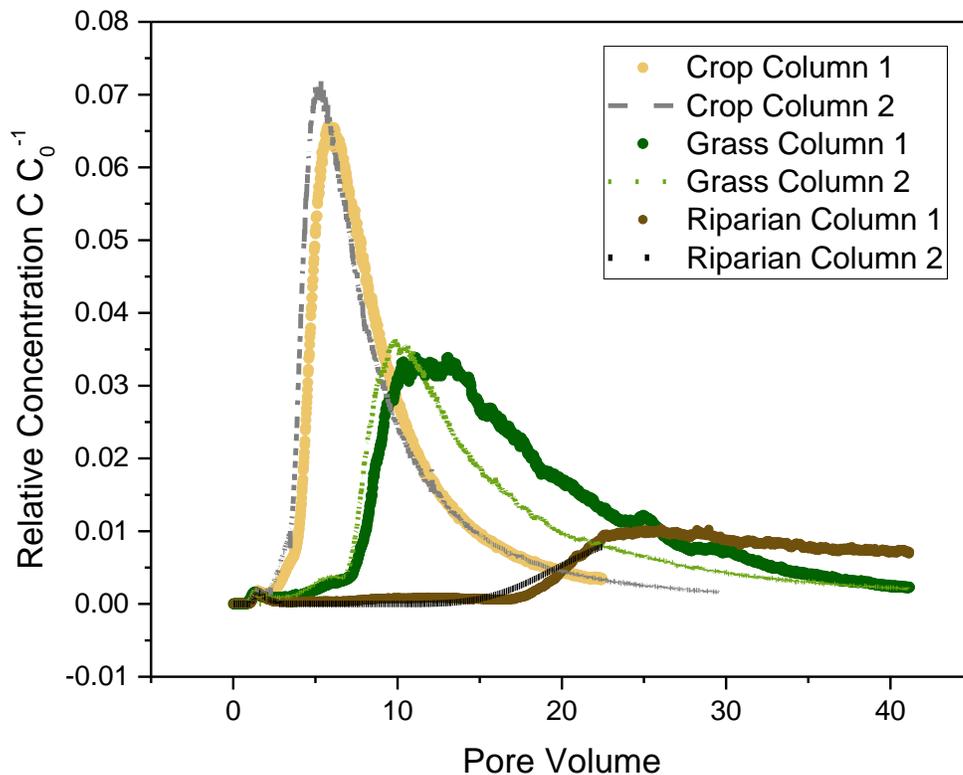
<sup>c</sup>  $v$ , ( $\text{cm h}^{-1}$ ) pore water velocity.

<sup>d</sup>  $\theta$ , ( $\text{cm}^3 \text{cm}^{-3}$ ) volumetric water content; measured.

<sup>e</sup>  $D$ , ( $\text{cm}^2 \text{h}^{-1}$ ) dispersion coefficient.

### 3.3.4 Imidacloprid Transport

None of the BTCs were fully completed (i.e., ICD relative concentration did not return to zero) during the experimental procedure for each soil. The cumulative mass recovery of ICD in the leachate fraction was 99.8% for the cropland column after 25 pore volumes, 98.1% for the grass VBS column after 41.2 pore volumes, and 62.5% for the riparian VBS column after 41.2 pore volumes. The average peak concentrations of ICD occurred at 5.83, 10.84 and 23.8 pore volumes for cropland, grass VBS and riparian VBS, respectively (Figure 3.5). Differences in the peak concentration and mass recovery can be explained by the greater  $K_d$  values for ICD in the grass VBS (11.4 L kg<sup>-1</sup>) and riparian VBS (20.1 L kg<sup>-1</sup>) than in cropland soil (4.98 L kg<sup>-1</sup>). Fernandez-Perez et al. (1998) found that greater ICD was retained in the soil containing the most soil carbon in a layered soil column leaching experiment, and they also attributed this to the greater  $K_d$  values associated with greater soil OC. Since no degradation products were detected in the leachate, we can assume greater than 99% of the added ICD did not degrade based on detection limits for the degradation products evaluated. The unrecovered ICD remained in the soil columns and can be assumed to be a slowly desorbing fraction of ICD. Tailing of the falling BTC limb occurred in all columns and was most apparent in the VBS columns, indicating non-equilibrium sorption, often explained by time-dependent sorption and hysteresis. Slow kinetic sorption of ICD was also observed in several studies by Oi (1999) and Walker et al. (1995). Oi (1999) attributed this to the increase in ICD  $K_{OC}$  values with increasing incubation time. In addition, Broznic et al. (2012) reported hysteresis in ICD desorption studies with hysteresis being more pronounced in soils with high OC content. Little variation is observed between replicate columns.



**Figure 3.5** Imidacloprid breakthrough curves for soil columns packed to cropland, a grass vegetative buffer strip (VBS) and a riparian VBS collected from Thomas Hill Reservoir.

### 3.3.5 Modeling Results

The Levenberg-Marquardt nonlinear minimization algorithm (Marquardt, 1963) was used to optimize the HYDRUS-1D model, which provides numerical solutions to the governing solute transport equations. The model was run with constant flux conditions, and the saturated hydraulic conductivity was experimentally determined to be  $2.89 \text{ mm h}^{-1}$ . Only two-site and three-site models are discussed, because one-site models did not predict ICD transport very well. Wehrhan et al. (2007) and Chu et al. (2013) modeled

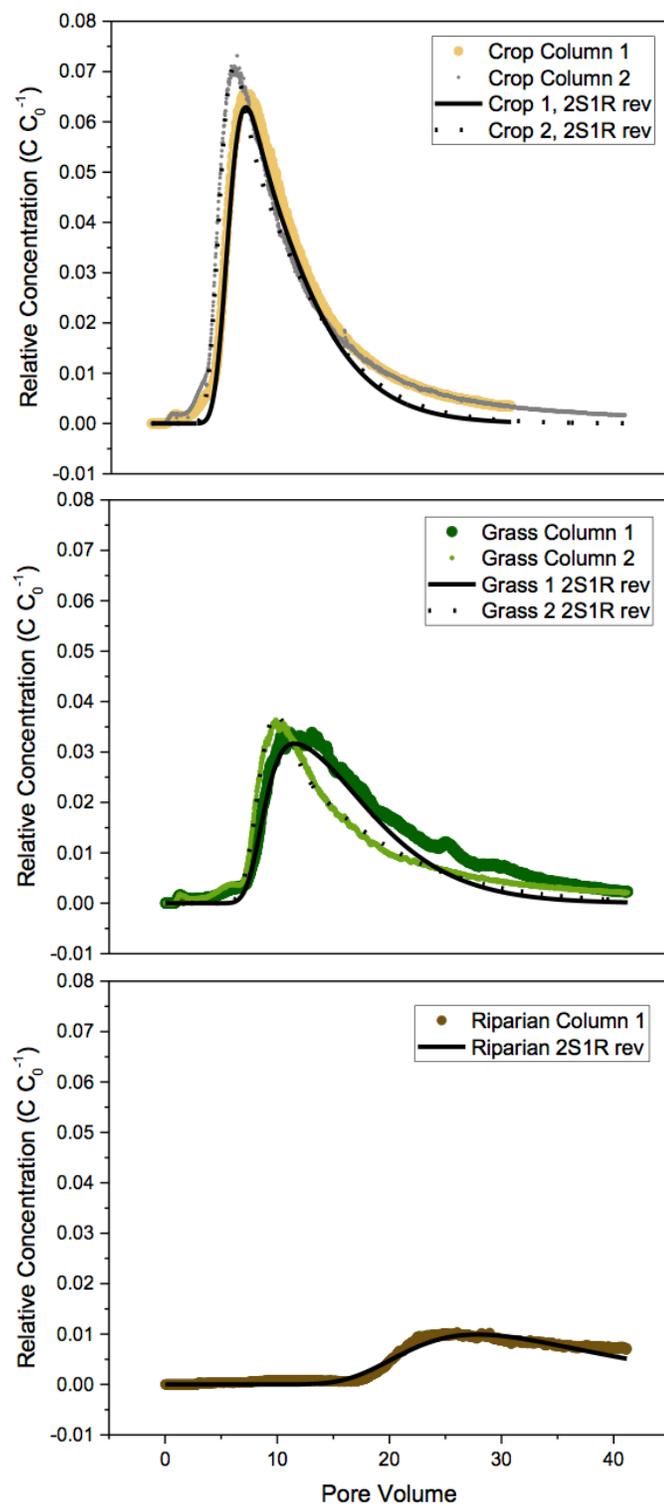
transport of veterinary antibiotics in soil columns also concluded that one-site models did not adequately describe transport.

The two-site, one-rate reversible (2S1R-rev) linear model fits are shown in Figure 3.6. The 2S1R-rev linear model best fit the BTC peaks and tailings, indicating ICD is mobile in soil due to the absence of irreversible sorption sites. The modeling efficiency (EF) values of the 2S1R-rev linear model were 0.996 and 0.995 for crop soil columns, 0.991 and 0.987 for grass VBS columns, and 0.965 for the riparian VBS column. The tail end of the grass and riparian soil column BTCs underpredicted ICD concentrations. We speculate more than two rates of sorption are occurring. Chu et al. (2013) also found a decrease in model fit from cropland soil to grass VBS and agroforestry (tree-grass) soil, indicating the current models do not account for complexities, such as more than two sorption rates, occurring in soils with greater carbon content.

The 3S2R-rev linear model EF values are only slightly less than the 2S1R-rev linear model EF values. We postulate 2S1R-rev linear is the better fit model, because our experimental data indicates all reversible sorption; the ICD concentration never returned to zero after 25 to 41.2 pore volumes and the crop columns leached nearly all the ICD (99.8%). In addition, the 3S2R-irrev model possibly overfits the BTCs; both models'  $f$  and  $\alpha_2$  values do not greatly differ and 3S2R-irrev's  $\beta_3$  values are very slow.

Mechanistic explanations for the nature of sorption sites associated with 2S1R-rev linear model must be explained by the relationship between land management and sorbate chemical structure. We speculate that instantaneous sorption sites (site 1) may be attributed to ICD sorption on soil minerals and partitioning into easily accessible portions of soil organic matter. Based on Liu et al. (2002) we postulate sorption mechanisms

contributing to site 1 occur on the clay by forming a hydrogen bond with the N=N group of the imidazolidine group or a cation bridge with the C=N group in the pyridine ring. We predict site 2 sorption occurs within tortuous pores, hydrophobic domains in soil organic matter, followed by ICD incorporation into organic matter. The sorption mechanisms attributable to site 2 most likely occur on the humic acids by forming a hydrogen bonds with the N=N group of the imidazolidine ring or C=N group of the pyridine ring. In addition, sorption may occur on the pyridine ring to SOM via hydrophobic forces (Zhu et al., 2003). However, we speculate that ICD remains mobile due to weak sorptive forces and high water solubility.



**Figure 3.6** Imidacloprid breakthrough curves and fitted 2-sites, 1-rate reversible model from soil columns packed to (a) cropland soil, (b) a grass vegetative buffer strip (VBS) and (c) a riparian vegetative buffer strip.

### 3.3.6 Parameter estimation

The fitted parameters for ICD sorption and transport are listed in Table 3.8. The estimated  $K_d$  values ranged from 3.78 to 23.1 L kg<sup>-1</sup>. These results follow a similar range to our data (4.98 to 20.1 L kg<sup>-1</sup>) from the sorption experiment and the reported  $K_d$  values in the literature (Cox et al. 1997). On average the 2S1R-rev and 3S2R-irrev linear models best predicted the cropland and grass VBS soil  $K_d$  values. The 2S1R-irrev and 2S2R-irrev linear models under predicted the cropland and grass VBS soil  $K_d$  values. Models including both site 1 and site 2 (2S1R-rev and 3S2R-irrev) better predicted the  $K_d$  values than models excluding site 1 or site 2 (2S1R-irrev and 2S2R-irrev), indicating the importance of both site 1 and site 2 in our soil.

The fraction of instantaneous sorption site ( $f$ ) values ranged from 58.6 to 76.7% of the total sorption sites for the 2S1R-rev model (Table 3.8), suggesting that a large portion of ICD is sorbed to the soil instantaneously. The estimated reversible sorption rate ( $\alpha_2$ ) was fastest in the cropland columns (0.023 h<sup>-1</sup> and 0.020 h<sup>-1</sup>) and slowest in the riparian column (7.76 x 10<sup>-3</sup> h<sup>-1</sup>) indicating greater retention of ICD in VBS columns and different sorption mechanisms associated with ICD interactions with site 2. This implies ICD is more bioavailable in cropland compared to the VBS soil. We speculate the absence of site 3 in the best fit model is due all reversible ICD sorption mechanisms. This can be explained by the high-water solubility of ICD; however strong, but reversible sorption mechanisms occurring as site 2 slow ICD transport.

**Table 3.8** Model efficiency (EF) and fitted parameters of different isotherm-based models obtained by HYDRUS-1D for five imidacloprid columns (all models are linear).

| Soil            | Model      | Batch $K_d$                        | Estimated $K_d$                    | $f^a$ | $\alpha_2^b$          | $\beta_3^c$           | EF    |
|-----------------|------------|------------------------------------|------------------------------------|-------|-----------------------|-----------------------|-------|
|                 |            | L kg <sub>soil</sub> <sup>-1</sup> | L kg <sub>soil</sub> <sup>-1</sup> |       | h <sup>-1</sup>       | h <sup>-1</sup>       |       |
| Cropland 1      | 2S1R-rev   | 4.98                               | 5.355                              | 0.657 | 0.023                 | 0                     | 0.996 |
|                 | 2S1R-irrev |                                    | 4.334                              | 1     | 0                     | 0.038                 | 0.765 |
|                 | 2S2R-irrev |                                    | 4.774                              | 0     | 0.115                 | 6.78x10 <sup>-6</sup> | 0.923 |
|                 | 3S2R irrev |                                    | 5.351                              | 0.657 | 0.024                 | 2.42x10 <sup>-6</sup> | 0.995 |
| Cropland 2      | 2S1R-rev   | 4.98                               | 5.179                              | 0.597 | 0.020                 | 0                     | 0.995 |
|                 | 2S1R-irrev |                                    | 3.778                              | 1     | 0                     | 0.045                 | 0.732 |
|                 | 2S2R-irrev |                                    | 4.399                              | 0     | 9.21x10 <sup>-2</sup> | 1.99x10 <sup>-4</sup> | 0.911 |
|                 | 3S2R irrev |                                    | 4.934                              | 0.611 | 0.024                 | 8.57x10 <sup>-6</sup> | 0.994 |
| Grass VBS<br>1  | 2S1R-rev   | 11.4                               | 11.512                             | 0.610 | 0.013                 | 0                     | 0.990 |
|                 | 2S1R-irrev |                                    | 9.714                              | 1     | 0                     | 3.62x10 <sup>-2</sup> | 0.631 |
|                 | 2S2R-irrev |                                    | 11.256                             | 0     | 11.764                | 0.0008                | 0.957 |
|                 | 3S2R irrev |                                    | 11.145                             | 0.620 | 0.014                 | 2.89x10 <sup>-6</sup> | 0.985 |
| Grass VBS<br>2  | 2S1R-rev   | 11.4                               | 11.401                             | 0.586 | 0.008                 | 0                     | 0.987 |
|                 | 2S1R-irrev |                                    | 7.839                              | 1     | 0                     | 4.89x10 <sup>-2</sup> | 0.763 |
|                 | 2S2R-irrev |                                    | 10.705                             | 0     | 36.916                | 0.003                 | 0.914 |
|                 | 3S2R irrev |                                    | 11.419                             | 0.585 | 0.008                 | 1.03x10 <sup>-5</sup> | 0.986 |
| Riparian<br>VBS | 2S1R-rev   | 20.1                               | 23.084                             | 0.767 | 7.76x10 <sup>-3</sup> | 0                     | 0.965 |
|                 | 2S1R-irrev |                                    | 20.743                             | 1     | 0                     | 1.52x10 <sup>-2</sup> | 0.875 |
|                 | 2S2R-irrev |                                    | 21.592                             | 0     | 5.78x10 <sup>-2</sup> | 2.19x10 <sup>-3</sup> | 0.933 |
|                 | 3S2R irrev |                                    | 23.077                             | 0.766 | 7.79x10 <sup>-3</sup> | 1.11x10 <sup>-6</sup> | 0.964 |

<sup>a</sup> $f$ : fraction of instantaneous sorption sites

<sup>b</sup> $\alpha_2$ : the reversible adsorption/desorption rate

<sup>c</sup> $\beta_3$ : the irreversible adsorption rate

### 3.4 Conclusions

This study demonstrates enhanced ICD soil sorption and retention under VBS management due to differences in physical and chemical properties between VBS and cropland soils. Sorption experiments resulted in greater  $K_d$  values in VBS soil due to greater organic carbon and nitrogen content. Column leaching studies determined greater retention of ICD in VBS columns and evidence for irreversible sorption in riparian VBS.

The 2S1R-rev and 3S2R-irrev models best fit the BTCs, and reflected the impact of vegetation treatment on the chemical nature of SOM and the complex nature of ICD sorption to soil. These results indicated that cropland SOM has reduce sorption affinity for ICD, leading to greater mobility in the environment. In contrast, riparian VBS soils showed significantly greater sorption of ICD than cropland soil, demonstrating the ability of riparian soils to reduce ICD bioavailability and hydrologic transport. These results also provide additional support for the importance of maintaining soil health and its link to the quantity and quality of SOM. Depletion of SOM in cropland soils reduces soil quality and in the context of this study, the ecosystem service of contaminant removal and remediation, by quantifiable reductions in ICD sorption. Further studies should investigate (1) plants within VBS ability to uptake ICD and potential to expose untargeted organisms (2) practices that increase OC in cropland soils and conducting studies investigating their ability adsorb ICD, and (3) and identifying microbial populations that promote ICD degradation, such as microbes present in tobacco fields. Ultimately, this research will aid in developing management guidelines for practitioners wishing to use VBS to mitigate ICD loss from agroecosystems.

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## Chapter 4.0 Conclusions

The main goals of this study were to investigate the sorption and retention of imidacloprid (ICD) in Missouri soils planted to vegetative buffer strips (VBS) and row-crops; determine the soil physical and chemical properties governing ICD sorption to soil; and model the transport processes of ICD through soil columns repacked with cropland, grass VBS and riparian VBS soil.

Results from the ICD sorption study (Chapter 3) demonstrated that the  $K_d$  values for ICD were significantly greater in soil under riparian VBS management than cropland soils. Organic carbon content was the most significant soil parameter influencing the ICD sorption, and organic carbon content was generally found to be higher in soils under VBS management.

Results from the column transport of ICD (Chapter 3) suggested that the majority of ICD can be leached through soil under saturated and constant flow conditions. However, after 25 and 45 days for cropland and VBS columns a small portion remained in the columns, indicating a fraction of ICD is slowly transported through the soil. The riparian VBS soil retained ICD the longest, followed by the grass VBS and cropland soil. A number of two-site and three-site models were applied to the transport data, and the best fitted model (2S1R-rev) assumes two different sorption sites: an instantaneous reversible sorption site and a rate-limited reversible sorption site. The 2S1R-rev model can best fit the BTCs of ICD in all three soil columns with model efficiency values of >99% (cropland), >98% (grass VBS) and >96% (riparian VBS). The decreased EF values for grass and riparian VBS suggest transport models can be improved to better predict transport parameters in soils under VBS management.

This study demonstrates that VBS buffers have better ability to retain ICD in soil than cropland. These current findings support evidence that VBS management is a practical way to prevent agrichemical loss to surface waters. However, there is concern VBS species may uptake ICD and expose untargeted organisms. Further studies should investigate (1) plants within VBS ability to uptake ICD and potential to expose untargeted organisms (2) practices that increase OC in cropland soils and conducting studies investigating their ability to adsorb ICD (3) and identifying microbial populations that promote ICD degradation, such as microbes present in tobacco fields. Ultimately, this research will aid in developing management guidelines for practitioners wishing to use VBS to mitigate ICD loss from agroecosystems.