Imidacloprid Sorption and Transport in Cropland, Grass Buffer, and Riparian Buffer Soils

Laura E. Satkowski, Keith W. Goyne,* Stephen H. Anderson, Robert N. Lerch, Elisabeth B. Webb, and Daniel D. Snow

An understanding of neonicotinoid sorption and transport in soil is critical for determining and mitigating environmental risk associated with the most widely used class of insecticides. The objective of this study was to evaluate mobility and transport of the neonicotinoid imidacloprid (ICD) in soils collected from cropland, grass vegetative buffer strip (VBS), and riparian VBS soils. Soils were collected at six randomly chosen sites within grids that encompassed all three land uses. Single-point equilibrium batch sorption experiments were conducted using radio-labeled ($^{14}$C) ICD to determine solid–solution partition coefficients ($K_d$). Column experiments were conducted using soils collected from the three vegetation treatments at one site by packing soil into glass columns. Water flow was characterized by applying Br$^-$ as a nonreactive tracer. A single pulse of $^{14}$C-ICD was then applied, and ICD leaching was monitored for up to 45 d. Bromide and ICD breakthrough curves for each column were simulated using CXTFIT and HYDRUS-1D models. Sorption results indicated that ICD sorbs more strongly to riparian VBS ($K_d = 22.6$ L kg$^{-1}$) than crop ($K_d = 11.3$ L kg$^{-1}$) soils. Soil organic C 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 soils, 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 soils than the cropland soil suggests that VBS may be a viable means to mitigate ICD loss from agroecosystems, thereby preventing ICD transport into surface water, groundwater, or drinking water resources.

Current agriculture practices are dependent on a class of insecticides, the neonicotinoids. In 2008, approximately 907 Mg of imidacloprid (ICD) and other neonicotinoids were applied to 58 million ha of US lands (Pilatic, 2012). These chemicals are valued for their low mammalian toxicity (Tomizawa and Casida, 2005), versatility of application (Jeschke et al., 2011), 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 seed coat application, neonicotinoids have the potential to negatively impact the behavior, survival, and populations of non-target organisms (Henry et al., 2012; Whitehorn et al., 2012; Douglas et al., 2015; Hallmann et al., 2014).

Studies have reported ICD concentrations of 0.09 to >100 µg kg$^{-1}$ in a variety of soils treated with ICD (Bonmatin et al., 2005; Jones et al., 2014). For example, ICD concentrations ranged from 17.5 to 59.6 µg kg$^{-1}$ in the top 10 cm of the soil after 4 yr of applying 133 g ICD ha$^{-1}$ (European Food Safety Authority, 2006). Because ICD does not rapidly degrade, it may persist and may accumulate in soils; thus, the time between planting seasons may not be adequate for neonicotinoid dissipation in soil (Bonmatin et al., 2008).
The hydrologic transport of a compound to surface or groundwater systems is largely influenced by its sorption to soil. Reported ICD solid–solution partition coefficient ($K_d$) values in a silt loam soil range from 1.4 to 14.4 L kg$^{-1}$ (Cox et al., 1997). Many studies agree that soil organic matter content (SOM) or organic C (OC) content is the strongest predictor of ICD sorption values (Cox et al., 1998a; Fernández-Pérez et al., 1998; Liu et al., 2006; Broznić et al., 2012); however, soil texture and cation exchange capacity (CEC) have also been found to be significant predictors of ICD $K_d$ values (Cox et al., 1997, 1998a, 1998b; Liu et al., 2006; Jeong and Selim, 2011; Broznić et al., 2012). Several studies found pH to be an insignificant predictor of ICD sorption, which is consistent with the fact that ICD is a neutral molecule in the typical soil pH range (Cox et al., 1998b; Broznić et al., 2012).

Liu et al. (2002) elucidated ICD sorption mechanisms by obtaining infrared spectra after ICD sorption on Ca-saturated clay minerals and humic acid–clay complexes. The spectra suggested that ICD sorbs to clay minerals through water bridging between the N=N group of the imidazolidine ring and hydrated cations of clay minerals and between coordination bonds between the C=N group of the pyridine ring and exchangeable cations on the mineral surface. Spectra also indicated that the N=N and C=N functional groups of ICD can form hydrogen bonds with the hydroxyl groups of humic acid.

Few studies evaluating ICD transport are found in the literature. Scorza et al. (2004) monitored ICD transport in a clay soil planted to winter wheat (Triticum aestivum L.) for 1 yr and observed greater ICD concentration in the upper 10 cm of soil after 189 d. After soil plowing, transport was indicated after Day 328, when the ICD concentration was greatest in the 10- to 20-cm layer. Downward movement of ICD was attributed to mixing of the soil from plowing, and the researchers concluded that 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 they concluded that ICD has a low leaching potential in soil with elevated SOM content. In comparison, the column leaching experiments of Gupta et al. (2002) illustrated that ICD has a greater potential to leach to groundwater in soil with reduced SOM. These studies (Fernández-Pérez et al., 1998; Gupta et al., 2002) provided additional support for the importance of SOM to ICD sorption and mobility in soils and suggest the need for additional research to better determine the sensitivity of ICD to SOM changes resulting from different land uses or conservation practices.

Previous research has illustrated the ability of vegetation to reduce ICD mobility (Peterson, 2007; Hladik et al., 2017). For example, Hladik et al. (2017) observed reductions in neonicotinoid transport from agricultural fields when strips of prairie grasses were established on the footslope position of fields. 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 nonpoint source agrochemical pollutant transport via physical, chemical, and biological mechanisms (Lowrance et al., 1997). Vegetative buffer strips have been shown to effectively reduce sediment, nutrient, pesticide, and veterinary antibiotic transport via surface runoff by increasing infiltration, adsorption to vegetation and soil, and sediment trapping (Misra et al., 1996; Udawatta et al., 2002; Blanco-Canqui et al., 2004; Lin et al., 2011; Chu et al., 2013b; Lerch et al., 2017). In addition, VBS enhance organic pollutant degradation by stimulating soil microbial activity (Mandelbaum et al., 1995; Lin et al., 2003, 2008, 2011) and by the production and release of degradative phytochemicals, such as benzoxazinones, into the rhizosphere (Lin et al., 2011; Willett et al., 2013, 2016). Soils within VBS typically contain greater soil organic C (SOC) content (Mandelbaum et al., 1995), and neonicotinoid sorption is generally enhanced in soils with greater SOC (Cox et al., 1998a; Rodríguez-Liébana et al., 2013). Therefore, the known effects of VBS on soil properties should result in reduced bioavailability to untargeted organisms and reduce the hydrologic transport of ICD and other neonicotinoids to surface and groundwaters.

To date, no published studies have investigated neonicotinoid sorption or modeled neonicotinoid transport in VBS soils. Although some studies have investigated ICD fate and transport in soil, sorption mechanisms and the influence of vegetation management on ICD transport in soil is not well understood. In this study, we used a combination of direct soil measurements and chemical nonequilibrium transport modeling to study ICD fate and transport. The specific objectives of this research were to: (i) examine ICD sorption to cropland, grass VBS, and riparian VBS soils; (ii) study ICD transport in soils from the three vegetation treatments; and (iii) fit ICD transport data to selected models to determine ICD sorption mechanisms and the potential for transport in soil.

Materials and Methods

**Sampling Sites, Soil Sampling, and Soil Characterization**

Sampling sites were chosen from public conservation areas managed by the Missouri Department of Conservation and located within 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 10.0.2) was used to overlay a grid of cells (300 by 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 and grassland and riparian buffers. From >100 cells each containing the three vegetation types, a total of six field sites were randomly selected for sampling. A description of the sites is 
Provided in the Supplemental Material (Supplemental Table S1). At each of the six sites, soil (4–5 kg) was randomly collected from the 0- to 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 to 50 cm from the base of trees to avoid larger roots. 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 parameters using methods (provided in parentheses) described in Soil Survey Laboratory Staff (2004): particle size distribution (pipette); exchangeable bases (unbuffered NH₄Cl); CEC (calculated by summation of cations exchanged in NH₄Cl); OC and total N contents (Leco C/N analyzer); and soil pH in water and salt (1:1 solid/solution ratio in water and 1:2 solid/solution ratio in 0.01 M CaCl₂, respectively). Soil property data for the sampling sites are shown in Table 1.

**Residual Neonicotinoid Concentrations**

The concentrations of residual neonicotinoid insecticides (ICD, acetamiprid, clothianidin, dimethoate, dinofuran, metalaxyl, thiacloprid, and thiamethoxam) in the soil samples studied were determined by microwave-assisted solvent extraction followed by liquid chromatography–tandem mass spectrometry (LC-MS/MS; Waters Model 2695 high-performance liquid chromatography [HPLC] system combined with a Quattro Micro triple quadrupole mass spectrometer). The method was validated according to standard protocols for analysis of environmental contaminants (USEPA, 1986), and the extraction and instrumental conditions are similar to previously published methods (Coscollà et al., 2009; Snow et al., 2013). All analyses were conducted at the University of Nebraska Water Sciences Laboratory (Lincoln, NE). High-purity methanol and other reagents were purchased from Fisher Scientific, and reference standards and isotopically labeled internal standards (clothianidin-d₃, imidacloprid-d₄, thiamethoxam-d₃, and metalaxyl-d₆) obtained from Sigma-Aldrich. Additional details of sample processing are included in the Supplemental Material. Residual neonicotinoid insecticide concentrations in the soil samples studied are presented in Table 1.

**Sorption Experiment**

Radio-labeled (¹⁴C) ICD [pyridyl 2,6-¹⁴C] (8.214 MBq mg⁻¹ ICD) was purchased from the Institute of Isotopes Co. (Budapest). Chemical properties are shown in Supplemental Table S2. Seven grams of air-dried soil was placed in 50-mL polypropylene centrifuge tubes and suspended in 35 mL of 0.01 mol L⁻¹ (ionic strength) CaCl₂ background electrolyte solution to achieve a 1:5 (w/v) soil/solution ratio. The use of CaCl₂ at

<table>
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<th>Site Location</th>
<th>Land management</th>
<th>Soil texture</th>
<th>Clay Silt</th>
<th>Organic C</th>
<th>Total N</th>
<th>CEC†</th>
<th>pHw‡</th>
<th>Total neonicotinoid§</th>
<th>Imidacloprid¶</th>
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<td>2.01</td>
<td>17.9</td>
<td>5.9</td>
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† Cation exchange capacity.
‡ pH in water.
§ Summation of residual imidacloprid, acetamiprid, clothianidin, dimethoate, dinofuran, metalaxyl, thiacloprid, and thiamethoxam extracted from each sample.
¶ LOD, limit of detection.
this approximate ionic strength is recommended for sorption studies due to the salt concentration being comparable to the average soil solution (Novozamsky et al., 1993; Organisation for Economic Cooperation and Development, 2000). Sufficient 14C-ICD was added to achieve 100 μg kg⁻¹ soil based on measured field soil concentrations ranging from <0.1 to >100 μg kg⁻¹ (Bonmatin et al., 2005). To ensure detection, the high end of observed ICD field concentrations was evaluated in this study. The residual concentration of ICD in the field samples was below the limit of detection or <10% of the applied ICD with the exception of one soil: Bunch Hollow cropland had a residual ICD concentration equivalent to 13% of the applied ICD (Table 1). To inhibit microbial degradation, (S) after reaction, Vₘ (corresponding to concentrations of 0–17 μM ICD), and adsorbent-free controls (no soil) were reacted in triplicate. Reaction tubes were centrifuged at 13,000 rpm for 15 min following the reaction period. The supernatant solution was filtered through a 0.45-μm nominal pore size polytetrafluoroethylene membrane filter, and 1 mL of solution was added to 4 mL of liquid scintillation cocktail (PerkinElmer UltimaGold AB). Samples were counted for 10 min or until reading converged within 2% of each other on a Beckman LC 6000SC liquid scintillation counter (LSC). A calibration curve was created for the LSC method by spiking the CaCl₂–NaN₃ solution with known 14C-ICD concentrations ranging from 0 to 140.6 μCi L⁻¹ (corresponding to concentrations of 0–17 μg L⁻¹).

The amount of ICD adsorbed to the soil after reaction was calculated using

\[
q_{\text{ads}} = \frac{C_{\text{ads,B}} V_B - C_{\text{ads,S}} V_S}{m_s}
\]  

where \(q_{\text{ads}}\) is the surface excess of ICD (i.e., amount adsorbed) after the reaction period (μmol kg⁻¹), \(C_{\text{ads,B}}\) and \(C_{\text{ads,S}}\) are the equilibrium ICD concentrations (μmol L⁻¹) in the blank (B) and samples (S) after reaction, \(V_B\) and \(V_S\) are the volumes of solution (L) added to the blanks (B) and samples (S), and \(m_s\) is the mass of soil (kg) added to the reaction vessel (Essington, 2015). The solid–solution partition coefficient (\(K_d\)) was calculated by dividing \(q_{\text{ads}}\) by \(C_{\text{ads,S}}\).

Analysis of variance with Duncan’s multiple range test was used to analyze the \(K_d\) data using SAS (SAS Institute) for a randomized complete block design with six blocks (sites) and three vegetative treatments (cropland, grass VBS, and riparian VBS). Statistical differences were tested at α = 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 in SAS.

**Leaching Experiment**

Soil from Thomas Hill Reservoir Conservation Area was chosen for the leaching experiment due to noticeable differences in \(K_d\) values among soil treatments. The general experimental setup and procedures used in the leaching experiments followed those of Chu et al. (2013a). Glass columns (inner diameter of 7.5 cm and length of 15 cm) were custom made of durable glass with polyethylene end caps and fittings (Kimble Chase). A layer of nylon Nitex mesh (10-μm nominal opening) was placed on the bottom end caps of each column to retain soil. Glass beads (0.8–1.2 mm), heat treated at 400°C for 24 h, were packed to a 3-cm depth on the Nitex mesh to fill the tapered column end. A 0.5-cm layer of quartz sand was placed on top of the glass beads and leveled. Air-dried soil passed through a 1-mm mesh sieve was packed to a height of 10.5 cm and a bulk density of 1.1 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. A schematic diagram of the column is provided in Supplemental Fig. S1. The columns were prepared in duplicate for each vegetative management system (i.e., cropland, grass VBS, and riparian VBS).

Each soil column was gradually saturated with CaCl₂ solution (\(I = 0.01\) mol L⁻¹) containing 1.5 mM NaN₃ from bottom to top (upward) during a 48-h time period. After saturation of the column, the CaCl₂–NaN₃ solution was added to the top of the column using a Masterflex L/S pump, and a fraction collector (Teledyne Isco Foxy 200) was used to collect leachate from a sampling port located at the bottom of the column. The soil column was irrigated with the CaCl₂–NaN₃ solution at a rate of 0.25 cm h⁻¹ (Darcy flux) to establish a steady flow rate that was confirmed by monitoring of leachate fraction volumes. Upon the establishment of constant water flow, a 2-h pulse of Br⁻ tracer (8.4 mM KBr) was applied and eluted with CaCl₂–NaN₃ 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 evaporative loss and monitor leachate volume. The concentration of Br⁻ in each leachate fraction was measured using a Dionex ICS-1000 ion chromatograph equipped with a IonPac AS14A (4 by 250 mm) anion column and an AS40 autosampler (Dionex Corp.). Solution eluent (Dionex AS14A Eluent Concentrate) was pumped at a flow rate of 1.0 mL min⁻¹ and standards (Dionex Combined Seven Anion Standard II) ranging from 0 to 500 μM Br⁻ were used to create a standard curve. Bromide concentrations were normalized to the initial concentration (C₀), and Br⁻ breakthrough curves (BTCs) were determined for each repacked column to describe water flow behavior prior to ICD addition to estimate physical equilibrium transport parameters.

Radio-labeled ICD was diluted in CaCl₂ (\(I = 0.01\) M) solution containing 1.5 mM NaN₃ solution and applied to the column to achieve an ICD concentration of 100 μg ICD kg⁻¹ soil, resulting in a total addition of 419.21 kBq of 14C-ICD. The ICD solution was applied at the same flow rate as the Br⁻ tracer and pulsed into the columns for 10 h. The cropland, grass VBS, and riparian VBS columns were continuously irrigated with CaCl₂–NaN₃ solution for times ranging from 630 h (23.5 pore volumes) to 1100 h (41.2 pore volumes) at the same steady flow rate. The
Leachate fraction was collected and capped as described above for the Br\(^{-}\) tracer experiments.

Liquid scintillation counting was used to determine the activity and concentration of \( ^{14}\)C-ICD in the leachate, as described above. Leachate pH and ICD degradation products were measured in every 50th sample. Imidacloprid degradation products were monitored using a HPLC unit (Shimadzu) with a flow scintillation analyzer. A Zorbax Eclipse XDB C\(_{18}\) column (2.1 by 200 mm, 3.5 \(\mu\)m, Agilent Technologies) 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\(^{-1}\). The gradient method was as follows (A:B, \%): 98:2 from 0 to 1 min; ramp to 95:5 from 1 to 3 min; 95:5 held from 3 to 4 min; ramp to 2:98 from 4 to 5.5 min; 2:98 held from 5.5 to 6.5 min. Calibration standards (0–3.33 kBq mL\(^{-1}\)) were prepared by dilution of ICD stock solutions in Millipore water. The detection limit was determined to be 0.111 kBq mL\(^{-1}\).

Retention times were 2.37 min for imidacloprid guanidine (desnitro-imidacloprid hydrochloride), 2.45 min for 6-chloronicotinic acid (6-chloropyridine-3-carboxylic acid), and 2.56 min for ICD. The absence of ICD degradation product peaks in columns fortified with NaN\(_3\) was interpreted as the absence of biotic and abiotic ICD degradation.

**Transport Modeling**

Solute transport parameters were estimated for each column by solving the inverse problem using nonlinear least-squares optimization (Chu et al., 2013a). The computer program CXTFIT (Toride et al., 1995) was used to analyze Br\(^{-}\) BTCs and provide an estimate for physical transport parameters. Physical transport estimated parameters for Br\(^{-}\) were then input to the HYDRUS-1D computer program (Simůnek et al., 1998) to determine chemical transport processes for ICD. 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., 2013a). The model assumes that the sorbate concentration \((S)\) is the sum of the solute concentration \([\text{M solute M}^{-3}\text{total soil}]\) on (i) instantaneous sorption sites \((S_1)\), (ii) kinetic sorption sites \((S_2)\), and irreversible sorption sites \((S_3)\):

\[
S = S_1 + S_2 + S_3
\]  

Instantaneous sorption sites \((S_1)\) follow a linear relationship with the liquid-phase solute concentration:

\[
S_1 = fK_dC
\]  

Kinetic sorption sites \((S_2)\) follow a first-order kinetic sorption rate:

\[
\frac{dS_2}{dt} = \alpha_2 \left[\left(1 - f\right)K_dC - S_2\right]
\]

and irreversible sorption sites \((S_3)\) follow a first-order kinetic sink for liquid-phase solutes:

\[
\frac{\partial S_3}{\partial t} = -\beta_3C
\]

where \(f\) is the fraction of Type 1 sorption sites available for instantaneous sorption; \(C\) is the solute concentration \([\text{M L}^{-3}]\); \(t\) is time [T]; \(\alpha_3\) is the first-order sorption kinetic rate constant at the second adsorption site [T\(^{-1}\)]; \(\beta_3\) is the irreversible adsorption rate [T\(^{-1}\)]; and \(K_d\) is the solid–solution partition coefficient (Eq. [1]), which has been described above.

A three-site, two-rate irreversible model (3S2R-irrev) is created by combining Eq. [3–5]:

\[
\frac{\partial C}{\partial t} + \rho K_d C + \rho \alpha_2 \left[\left(1 - f\right)K_d C - S_2\right] + \theta \beta_3 C = 0
\]

where \(z\) is the depth and all other variables have been previously described (Jury and Horton, 2004). Omitting different sites permits the development of a variety of sorption models (Fig. 1).

**Fig. 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; \(S_1\) is an instantaneous sorption site, \(S_2\) is a kinetic sorption site, and \(S_3\) is an irreversible sorption site; \(K_d\) is the solid–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, flux density \( (q) \) was determined experimentally, and the soil water content \( (\theta) \) was assumed to be saturation. For Br\(^-\) modeling, CXTFIT-estimated transport parameters included the dispersion coefficient \( (D) \) and pore water velocity \( (v) \), and these parameters were used to calculate the dispersivity \( (\lambda = D/v) \). For ICD modeling, the estimated transport parameters included the \( K_d \), the reversible adsorption–desorption rate \( (\alpha_d) \), the fraction of instantaneous sorption sites \( (\beta_i) \), and the irreversible adsorption rate \( (\beta_d) \). The model efficiency \( (EF) \) was used as a measure of the goodness of the model fit:

\[
EF = 1 - \frac{\sum (O_i - P_i)^2}{\sum (O_i - O_{mean})^2}
\]

where \( O_i \) and \( P_i \) are the observed and predicted values, respectively, and \( O_{mean} \) is the arithmetic mean of the observed values (Nash and Sutcliffe, 1970). Greater \( EF \) values are indicative of better model fit to the BTCs.

**Results and Discussion**

**Solid–Solution Partition Coefficients**

Imidacloprid sorption was moderate to strong for all soils studied, ranging from 5 to 40 L kg\(^{-1}\), with an overall mean of 17.4 L kg\(^{-1}\). Evaluation of \( K_d \) shows ICD sorption is 

Cumulatively, the \( K_d \) data indicated that soils under riparian VBS management exhibit enhanced ICD sorption relative to cropland management at environmentally relevant concentrations and suggests that the sorptive capabilities of riparian VBS soils may help reduce neonicotinoid loss to agroecosystems. Similar to our results, Fernández-Pérez et al. (1998) reported increased ICD soil sorption in land management systems containing more soil C (peat and native vegetation) than little to no C (amended soil and no vegetation). To the best of our knowledge, this is the first report indicating the potential of VBS soils to sorb ICD to a greater extent than cropland soil and confirms that riparian vegetation provides ecosystem services, such as ICD retention and mitigation.

**Correlation of Sorption to Soil Properties**

The \( K_d \) values for ICD exhibited the strongest and most significant correlation with OC content and weaker correlations with total N, CEC, clay content and pH\(_{\text{water}}\) (Table 2); OC alone explained 81.9% of the observed variance (Fig. 3a). To further refine the relationships between ICD \( K_d \) values and soil properties, stepwise multiple regression analysis was used. Although total N was the second strongest predictor of ICD sorption, it was not included in the stepwise multiple linear regression due to collinearity with OC \( (r = 0.982) \), indicating that the variables were not independent. The inclusion of additional parameters (pH\(_{\text{water}}\) and CEC) in the model (Fig. 3b and 3c) resulted in slightly greater explanation of variance. Only 2.3% of additional variance was explained by adding pH\(_{\text{water}}\) compared with the OC-only model, which was probably due, in part, to the limited range of soil pH\(_{\text{water}}\) values (5.0–7.2) in the samples studied. Additionally, acid-dissociation constants \( (pK_a) \) of the functional groups on ICD (1.56 and 11.1) resulted in a neutral molecule across the soil pH\(_{\text{water}}\) range studied, which further limited the effect of pH on ICD sorption (Farenhorst, 2006). Inclusion of CEC in the stepwise multiple linear regression model explained an additional 1.2% of the variance over the model including OC and pH\(_{\text{water}}\).

Organic C has been reported by others as a strong predictor of ICD adsorption (Cox et al., 1998a; Koskinen et al., 2001; Broznić et al., 2012). When little to no OC was present in soil, CEC and soil texture were noted as good predictors of \( K_d \) values are comparable to ICD \( K_d \) values reported 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. Imidacloprid \( K_d \) values for grass VBS soils were intermediate and did not differ significantly from \( K_d \) values for cropland or riparian VBS soils \( (p = 0.312 \text{ and } 0.859, \text{ respectively}) \).

**Table 2. Linear correlation coefficients between imidacloprid solid–solution partition coefficients \((K_d)\) and soil properties.**

<table>
<thead>
<tr>
<th>Statistic</th>
<th>Organic C</th>
<th>Total N</th>
<th>Cation exchange capacity</th>
<th>Clay content</th>
<th>pH(_{\text{water}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R )</td>
<td>0.905</td>
<td>0.842</td>
<td>0.794</td>
<td>0.504</td>
<td>0.439</td>
</tr>
<tr>
<td>( p ) value</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>0.0328</td>
<td>0.0685</td>
</tr>
</tbody>
</table>

Fig. 2. Mean imidacloprid solid–solution partition coefficients \((K_d)\) for cropland, grass vegetative buffer strip (VBS), and riparian VBS soils collected at six sites in northern Missouri. Error bars represent one standard deviation.
for ICD (Fernández-Bayo et al., 2008). In a study of ICD adsorption to six soils, Broznić et al. (2012) and Liu et al. (2006) also observed that OC explained the greatest variance when a multiple regression analysis was performed. In addition, Li et al. (2006) observed SOM to explain the greatest variance in a study of ICD adsorption to six soils when a multiple regression analysis was performed. Results presented here were consistent with these studies and also showed that OC alone was a substantial predictor of ICD sorption to soils covering a broad range of OC concentrations (12.5–58.5 g kg\(^{-1}\)). There are no published studies investigating the alteration of SOM chemical structure at any of the six sites studied. However, spectroscopic studies of SOM have shown that land management practices influence SOM chemical structure (Condron and Newman, 1998; de Alcântara et al., 2004; Veum et al., 2012). We postulate that changes in SOM fractions and chemical composition within a VBS may play an important role in ICD sorption to the soils studied. A positive correlation of pH and CEC to ICD \(K_d\) values in the multiparameter models also correspond with previous research (Liu et al., 2006; Broznić et al., 2012). However, the models developed by Liu et al. (2006) and Broznić et al. (2012) included clay content, which was not found to be a significant factor on retention processes in our predictive models and particular experimental systems.

**Bromide Transport**

The BTCs of the conservative, anionic Br\(^{-}\) tracer describe water movement in each column containing soil from the Thomas Hill Reservoir site, allowing us to distinguish the effects of chemical nonequilibrium from physical nonequilibrium when comparing Br\(^{-}\) and ICD BTCs. The measured Br\(^{-}\) BTCs and model fits are shown in Fig. 4. The measured peak pore volume for each vegetative management system occurs slightly before one pore volume, indicating anion exclusion (Fig. 4). The soil columns were repacked (homogenized) with 1-mm sieved soil to ensure that advective transport processes were dominant (physical equilibrium resulted) to minimize or exclude effects due to macropores such as preferential flow.

All BTCs display concentration tailing for the falling (elu-

cation) limb of the curve; the riparian and grass VBS exhibited the most notable tailing behavior. In addition, the peak Br\(^{-}\) concentration of the riparian soil BTC was significantly less than the cropland and grass soil BTCs. We speculate that the tailing and reduced peak concentration were due to soil structure disparities and possibly anion adsorption in the riparian zone soil rather than physical nonequilibrium. Although the soil was sieved to 1 mm, riparian soil particles remained aggregated, while crop and grass VBS soils were less aggregated (visual observation). These observations of aggregation are in partial agreement with Veum et al. (2012), where agroforestry and grass VBS soils were found to contain more water-stable aggregates than no-till cropland soil. To our knowledge, no studies exist investigating Br\(^{-}\) transport in microaggregates (<3 mm). However, Nielsen and Biggar (1962) found that increasing aggregate size resulted in early appearance of the tracer during miscible displacement experiments, indicating the effect of preferential flow. Intra-aggregate pore distribution consists of finer and more tortuous pores, increasing the chemical flow path length (Horn et al., 1994).

Chu et al. (2013a) also found a reduced peak Br\(^{-}\) concentration in riparian soil using the same experimental design and
speculated that this was due to increased positive charge on the surface of Al and Fe oxides as well as from the presence of kaolinite in the riparian soil compared with the cropland soil. In this study, clays in the riparian zone soils would more likely be of mixed mineralogy (including kaolinite) than the grass VBS or cropland soils due to fluvial deposition of sediments along drainage pathways. The presence of variable-charge minerals in the riparian soil could facilitate anion adsorption; however, the near neutral pH of the Thomas Hill Reservoir soils studied here suggests that anion adsorption should be limited due to few positively charged functional groups. We postulate that microaggregation in the riparian VBS soil dispersed the Br\(^-\) to a greater extent than in the other treatments by a combination of preferential flow and slow tortuous pathways that resulted in both earlier detection of Br\(^-\) (via preferential flow paths) and extended detection of Br\(^-\) (via tortuous pathways) to create the observed BTCs. Therefore, a physical equilibrium, convection–dispersion equation was used to describe the Br\(^-\) BTCs, and the transport parameters \(D\) and \(v\) were fit using CXTFIT (Table 3).

**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 average cumulative mass recovery of ICD in the leachate fraction was 99.8% for the cropland column after 23.5 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 (due to experimental time constraints, cropland Column 1 and riparian Column 2 were run for 23.5 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 soils, respectively (Fig. 5; Supplemental Fig. S2). Little variation was observed between replicate columns. Differences in the peak concentration and mass recovery can be explained by the greater \(K_d\) values for ICD in the grass VBS \((11.4 \text{ L kg}^{-1})\) and riparian VBS soils \((20.1 \text{ L kg}^{-1})\) than in the cropland soil \((4.98 \text{ L kg}^{-1})\). Fernández-Pérez et al. (1998) found that greater ICD retention occurred in soil containing the greatest OC content in a layered soil column leaching experiment, and they attributed this to the greater \(K_d\) values associated with greater OC content. Because no degradation products were detected in the leachate, we can assume that <1% of the added ICD degraded 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 BTCs was observed for all columns and was most apparent in the VBS columns, indicating nonequilibrium sorption, often explained by time-dependent sorption and hysteresis, or effects on transportation due to aggregation causing a higher tortuous flow and diffusion constraints. 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 organic C–solution partition coefficient \((K_{OC})\) values with increasing contact time. Broznić et al. (2012) reported hysteresis in ICD desorption studies, with hysteresis being more pronounced in soils with greater OC content.

**Table 3.** Estimated parameters, including pore water velocity (\(v\), cm h\(^{-1}\)) and the dispersion coefficient (\(D\), cm\(^2\) h\(^{-1}\)), and experimentally measured conditions of flow rate (\(q\), cm h\(^{-1}\)), soil bulk density (\(p\), g cm\(^{-3}\)), and volumetric water content (\(\theta\), cm\(^3\) cm\(^{-3}\)) for cropland, grass vegetated buffer strip (VBS), and riparian VBS saturated column experiments.

<table>
<thead>
<tr>
<th>Column</th>
<th>(q)</th>
<th>(p)</th>
<th>(v)</th>
<th>(\theta)</th>
<th>(D)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cropland</td>
<td>0.23</td>
<td>1.1</td>
<td>0.566 (0.001)†</td>
<td>0.51</td>
<td>0.14 (0.003)</td>
<td>0.985</td>
</tr>
<tr>
<td>Grass VBS</td>
<td>0.23</td>
<td>1.1</td>
<td>0.512 (0.02)</td>
<td>0.47</td>
<td>0.12 (0.03)</td>
<td>0.943</td>
</tr>
<tr>
<td>Riparian VBS</td>
<td>0.23</td>
<td>1.1</td>
<td>0.615 (0.05)</td>
<td>0.56</td>
<td>0.2 (0.04)</td>
<td>0.874</td>
</tr>
</tbody>
</table>

† 95% confidence intervals are shown in parentheses.
Modeling Results

The Levenberg–Marquardt nonlinear minimization algorithm (Marquardt, 1963) was used to optimize the HYDRUS-1D model, which provided numerical solutions to the governing solute transport equations (the riparian VBS 2 column was incomplete and not included in the HYDRUS-1D simulations). The model was run with constant-flux conditions, and the saturated hydraulic conductivity was experimentally determined using a constant-head method to be 2.89 mm h$^{-1}$. Only two-site and three-site models are discussed because one-site models did not sufficiently predict ICD transport. Wehrhan et al. (2007) and Chu et al. (2013a) modeled transport of veterinary antibiotics in soil columns and also concluded that one-site models did not adequately describe transport. Only linear models were used because multipoint adsorption isotherm experiments were not conducted.

The 2S1R-rev (two-site, single-rate, reversible) linear model appeared to best fit the BTCs, accurately estimating the observed peaks and prolonged tailing observed for all three soil treatments (Table 4; Fig. 5). 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. However, the 2S1R-rev model consistently underestimated ICD concentrations at the tail of each BTC. This suggests that the model is either overestimating the reversible site sorption rates and/or more than two rates of sorption were occurring. Chu et al. (2013a) also found a decrease in model fit from cropland soil to grass VBS and agroforestry (tree–grass) soil. The reduced model fits indicate that the current models do not account for complexities (e.g., more than two reversible site sorption rates) that may occur in soils, particularly soils with greater OC content and a diversity of OC fractions that develop under perennial vegetation.

The 3S2R-irrev (three-site, two-rate, irreversible) linear model EF values were only slightly less than those for the 2S1R-rev linear models. This model includes irreversible ($S_3$) sorption sites, which was not consistent with the BTCs for crop and grass VBS treatments because they both asymptotically approached zero ICD concentration and >98% of applied ICD mass was recovered in the leachate (Supplemental Fig. S2). These trends suggested that reversible sorption sites with slow desorption kinetics were controlling ICD concentrations (and transport) during the tailing limb (elution) of these BTCs rather than irreversible sites. Results for the riparian BTC were more ambiguous because only 62.5% of the applied ICD mass was recovered, and ICD concentrations from 23.5 to 41.2 pore volumes remained steady and near that of the peak relative concentration of $0.01 C_0$ (Fig. 5; Supplemental Fig. S2). These results may have been due to reversible sites but with an even slower desorption rate than that observed for the crop and grass treatments. However, the possibility exists that a portion of the ICD in the riparian treatment was irreversibly sorbed and the 3S2R-irrev linear model may be applicable.

Mechanistic explanations for the nature of sorption sites associated with 2S1R-rev linear and 3S2R-irrev linear models can be explained by the relationship between SOC, because of differences in land management, and sorbate chemical structure. We speculate that $S_1$ sites may be attributed to ICD sorption on soil minerals and partitioning into easily accessible portions of SOC. Based on
Liu et al. (2002), we postulate that sorption mechanisms contribut-
ing to $S_1$ represent electrostatic and hydrogen bonds occurring at
the clay surface or with polar OC groups. Bonding mechanisms
include ion exchange (via protonation of the pyridine ring at the
colloid surface), formation of coordination bonds, water bridging,
and hydrogen bonding to clay mineral surfaces, as well as hydrogen
bonding to hydroxyl groups on the external surface of SOC. We
interpret $S_2$ sites to represent sorption occurring within tortuous
microaggregate pores and hydrophobic SOC domains in which
sorption equilibrium is reached slowly. The sorption mechanisms
attributable to $S_2$ may include mechanisms described above for $S_1$,
but they could also include hydrophobic partitioning between the
pyridine and/or imidazolidine rings and hydrophobic moieties of
SOC (Zhu et al., 2003). The $S_3$ sites are interpreted to repre-
sent some combination of physical or chemical entrapment of
ICD within tortuous pores and hydrophobic SOC domains and
incorporation of ICD into SOC by covalent bonding that greatly inhibits desorption (i.e.,
desorption is nearly irreversible or so kinetically slow as to appear irreversible). Overall, the
results indicated that ICD remains mobile in the soil due to weak sorption mechanisms that may
result in ICD release from soil surfaces and high water solubility of the neonicotinoid (2.01 mM)
that permits greater leaching potential.

### Parameter Estimation

The fitted parameters for ICD sorption and transport are listed in Table 4. The estimated $K_d$
values ranged from 3.78 to 23.1 L kg$^{-1}$ and exhibit a similar range to our sorption data
(4.98–20.1 L kg$^{-1}$) and $K_d$ values reported in the literature (Cox et al., 1997). Interestingly,
the model that always best fit overall transport (2S1R-rev) did not always best predict $K_d$
values compared with the experimentally determined $K_d$ values for the equilibrium batch experiments.
Only for the grass VBS columns was $K_d$ most closely predicted by 2S1R-rev.

The fraction of instantaneous sorption sites ($f$) ranged from 58.6 to 76.7% of the
total sorption sites for the 2S1R-rev model (Table 4), 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 and 0.020 h$^{-1}$) and slowest in the riparian column
(7.76 x 10$^{-3}$ h$^{-1}$) indicating greater retention of ICD in VBS columns and different sorption
mechanisms and/or kinetics associated with ICD interactions at $S_2$ sites. This indicates that
ICD is more mobile and bioavailable in crop-
land soil than VBS soils. For the riparian VBS
soil, the results did not allow distinguishing between retention
of ICD at $S_3$ sites or slow desorption from $S_2$ sites. However, the
overall results emphasize the importance of reversible, and possibly
irreversible, sites associated with SOC as the primary means of
controlling ICD transport in soil.

### Conclusions

This study demonstrated greater 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
SOC content. Results from the column leaching studies also dem-
onstrated the greater retention of ICD in VBS soil. The 2S1R-rev
and 3S2R-irrev linear models best fit the BTCs and reflected
the impact of vegetation treatment on the amount and chemical

#### Table 4. Model efficiency (EF) and fitted parameters of different linear sorption-based models
obtained by HYDRUS-1D for five imidacloprid columns containing cropland, grass vegetative
buffer strip (VBS), or riparian VBS soil. Solid–solution distribution coefficients ($K_d$ values)
were measured experimentally (batch $K_d$) and estimated by HYDRUS-1D.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Model†</th>
<th>Batch $K_d$</th>
<th>Estimated $K_d$</th>
<th>$f$‡</th>
<th>$\alpha_2$</th>
<th>$\beta_2$</th>
<th>EF§</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 L kg$^{-1}$ soil</td>
<td>h$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cropland 1</td>
<td>2S1R-rev</td>
<td>4.98</td>
<td>5.36</td>
<td>0.657</td>
<td>$2.30 \times 10^{-2}$</td>
<td>0</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>2S1R-irrev</td>
<td></td>
<td>4.33</td>
<td>1</td>
<td>0</td>
<td>3.80 $\times 10^{-2}$</td>
<td>0.765</td>
</tr>
<tr>
<td></td>
<td>2S2R-irrev</td>
<td></td>
<td>4.77</td>
<td>0</td>
<td>0.115</td>
<td>6.78 $\times 10^{-6}$</td>
<td>0.923</td>
</tr>
<tr>
<td></td>
<td>3S2R-irrev</td>
<td></td>
<td>5.35</td>
<td>0.657</td>
<td>$2.40 \times 10^{-2}$</td>
<td>2.42 $\times 10^{-6}$</td>
<td>0.995</td>
</tr>
<tr>
<td>Cropland 2</td>
<td>2S1R-rev</td>
<td>4.98</td>
<td>5.18</td>
<td>0.597</td>
<td>$2.00 \times 10^{-2}$</td>
<td>0</td>
<td>0.995</td>
</tr>
<tr>
<td></td>
<td>2S1R-irrev</td>
<td></td>
<td>3.78</td>
<td>1</td>
<td>0</td>
<td>4.50 $\times 10^{-2}$</td>
<td>0.732</td>
</tr>
<tr>
<td></td>
<td>2S2R-irrev</td>
<td></td>
<td>4.40</td>
<td>0</td>
<td>9.21 $\times 10^{-2}$</td>
<td>1.99 $\times 10^{-4}$</td>
<td>0.911</td>
</tr>
<tr>
<td></td>
<td>3S2R-irrev</td>
<td></td>
<td>4.93</td>
<td>0.61</td>
<td>$2.40 \times 10^{-2}$</td>
<td>8.57 $\times 10^{-6}$</td>
<td>0.994</td>
</tr>
<tr>
<td>Grass VBS 1</td>
<td>2S1R-rev</td>
<td>11.4</td>
<td>11.5</td>
<td>0.61</td>
<td>$1.30 \times 10^{-2}$</td>
<td>0</td>
<td>0.990</td>
</tr>
<tr>
<td></td>
<td>2S1R-irrev</td>
<td></td>
<td>9.71</td>
<td>1</td>
<td>0</td>
<td>3.62 $\times 10^{-2}$</td>
<td>0.631</td>
</tr>
<tr>
<td></td>
<td>2S2R-irrev</td>
<td></td>
<td>11.3</td>
<td>0</td>
<td>11.8</td>
<td>8.00 $\times 10^{-4}$</td>
<td>0.957</td>
</tr>
<tr>
<td></td>
<td>3S2R-irrev</td>
<td></td>
<td>11.1</td>
<td>0.62</td>
<td>$1.40 \times 10^{-2}$</td>
<td>2.89 $\times 10^{-6}$</td>
<td>0.985</td>
</tr>
<tr>
<td>Grass VBS 2</td>
<td>2S1R-rev</td>
<td>11.4</td>
<td>11.4</td>
<td>0.586</td>
<td>8.00 $\times 10^{-3}$</td>
<td>0</td>
<td>0.987</td>
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<tr>
<td></td>
<td>2S1R-irrev</td>
<td></td>
<td>7.84</td>
<td>1</td>
<td>0</td>
<td>4.89 $\times 10^{-2}$</td>
<td>0.763</td>
</tr>
<tr>
<td></td>
<td>2S2R-irrev</td>
<td></td>
<td>10.7</td>
<td>0</td>
<td>36.9</td>
<td>3.00 $\times 10^{-3}$</td>
<td>0.914</td>
</tr>
<tr>
<td></td>
<td>3S2R-irrev</td>
<td></td>
<td>11.4</td>
<td>0.585</td>
<td>8.00 $\times 10^{-3}$</td>
<td>1.03 $\times 10^{-3}$</td>
<td>0.986</td>
</tr>
<tr>
<td>Riparian VBS</td>
<td>2S1R-rev</td>
<td>20.1</td>
<td>23.1</td>
<td>0.767</td>
<td>7.76 $\times 10^{-3}$</td>
<td>0</td>
<td>0.965</td>
</tr>
<tr>
<td></td>
<td>2S1R-irrev</td>
<td></td>
<td>20.7</td>
<td>1</td>
<td>0</td>
<td>1.52 $\times 10^{-2}$</td>
<td>0.875</td>
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<td></td>
<td>2S2R-irrev</td>
<td></td>
<td>21.6</td>
<td>0</td>
<td>5.78 $\times 10^{-2}$</td>
<td>2.19 $\times 10^{-3}$</td>
<td>0.933</td>
</tr>
<tr>
<td></td>
<td>3S2R-irrev</td>
<td></td>
<td>23.1</td>
<td>0.766</td>
<td>7.79 $\times 10^{-3}$</td>
<td>1.11 $\times 10^{-6}$</td>
<td>0.964</td>
</tr>
</tbody>
</table>

† The model names represent the number of sites (S), number of rates (R), and reversibility of sorbate
‡ Fraction of instantaneous sorption sites.
§ Reversible adsorption–desorption rate.
¶ Irreversible adsorption rate.
# Model efficiency.
nature of SOM in the soils studied and the complex nature of ICD sorption to soil. These results indicated that cropland soil has reduced sorption affinity for ICD compared with the VBS treatments, leading to greater mobility and bioavailability 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. We acknowledge that evaluating ICD sorption and transport under saturated conditions does not fully mimic processes occurring within unsaturated or partially saturated soil conditions; however, our results do advance scientific understanding of ICD transport in the pedosphere. 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 SOC in cropland soils reduces soil quality and, in the context of this study, the ecosystem service of contaminant removal and remediation through quantifiable reductions in ICD sorption and transport. Therefore, installation of vegetative buffers along crop field borders and improved riparian management can effectively reduce the transport of ICD in agroecosystems.

Acknowledgments
This research was supported by a research grant from the Missouri Department of Conservation (MDC). Partial support was also provided by USDA-NIFA through Hatch funding (MO-HANR0007) and Multi-State Working Group W0945 (MO-MSNR0002). We thank the following individuals for their assistance: Do- reen Mengel and Craig Scroggins of MDC, Bettina Coggeshall from the USDA–ARS (retired); and Tristan Laughlin, Rachel Owen, and Alex Taylor of the University of Missouri. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the US Government.

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doi:10.1016/j.chroma.2009.10.040
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