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Herbicide and Antibiotic Removal by Woodchip Denitrification Filters: Sorption Processes

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Abstract In situ denitrification walls and biofilters made of wood chips are being implemented as innovative technologies for the removal of nitrates in tile drainage water from farms to reduce pollution of surface waters and the hypoxia problem in the Gulf of Mexico. Although fairly effective in removing nitrates, not much is known about the effectiveness of the biofilters in removal of herbicides, pesticides, and antibiotics in the drainage water. Using weathered wood chips obtained from an in situ denitrification wall, four common pollutants tested sorbed strongly to wood chips in the following order: enrofloxacin > monensin A > atrazine > sulfamethazine. Of the four chemicals tested, enrofloxacin was found to desorb the least by water extraction. The apparent hysteresis index for atrazine was found to be lower than that for enrofloxacin and sulfamethazine indicating greater sorption–desorption hysteresis for atrazine than enrofloxacin and sulfamethazine. Consecutive steps of water desorption and organic solvent extraction indicated that more than 65% of the sorbed atrazine, 70% of sulfamethazine, 90% of enrofloxacin, and 80% of monensin A were retained in wood chips. Results of this study showed that wood chip denitrification walls or biofilters have an added benefit in retaining herbicides and antibiotics and therefore can act as a barrier to reduce pollution of surface water and groundwater.

Keywords Atrazine · Sulfamethazine · Enrofloxacin · Monensin A · Denitrification wall · Wood chips · Sorption · Desorption

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1 Introduction

Many Midwest states in the USA suffer from nitrogen and phosphorus pollution of surface and ground waters due to heavy use of fertilizers and manure. In some states, the nutrients are rapidly conveyed to open bodies of water by the tile drainage systems which, ironically, were constructed to improve water drainage and increase agricultural yield. Various management strategies such as denitrification walls and wood chip bioreactors have been applied to reduce nitrate in drainage and ground waters where nitrate in water is reduced by

denitrifying microorganisms. Denitrification walls and wood chip bioreactors, constructed with a mixture of sand and organic carbon sources, such as sawdust, cornstalks, or wood chips, variably removed NO_3^--N in drainage water, depending on the organic carbon to nitrogen ratio (Robertson and Cherry 1995; Schipper and Vojvodić-Vuković 1998) and the water flow rate (Greenan et al. 2009).

In addition to nitrate, other chemicals applied to the fields, such as pesticides, herbicides, and antibiotics in manure, may also leach into the subsurface drainage water and pollute surface and subsurface waters. For example, Kalita et al. (2006) monitored both atrazine and NO_3^--N in a watershed at four different locations in east central Illinois from 1991 to 2003 and found concentrations ranging from 0.87 to 1.22 μg $L^{-1}$and 15–20 mg L^{-1}, respectively. Measured atrazine concentrations in tile drainage water ranged from 1.3 to 5.1 μg L^{-1} by Jayachandran et al. (1994) which were close to atrazine concentrations detected (3 and 10 μg L^{-1}) in surface waters of Midwest states (Battaglin et al. 2003). Besides pesticides, antibiotics present in manure, such as sulfonamides, fluoroquinolones, and ionophores, have been found in ground water and surface waters (Boxall et al. 2003).

Pesticide and veterinary antibiotics contamination of ground and surface waters are of great concern due to their potential impacts on both aquatic and terrestrial ecosystems (Garner et al. 1986; Halling-Sørensen et al. 1998; Kolpin et al. 2002) and microbial resistance development (Teuber 2001). From the human health perspective, presence of antimicrobials in the ecosystem may result in the development of antibiotic resistant microbial strains (Martinez 2009) which may reduce the effectiveness of current treatments on zoopathogens. From the ecosystem health perspective, major concerns of pesticides and antibiotics are toxic effects of these chemicals on organisms. The adverse effects of enrofloxacin and sulfamethazine on the growth of many aquatic organisms such as *Daphnia* have been reported (Robinson et al. 2005; Kim et al. 2007). Pesticides such as atrazine may be endocrine disrupters as observed in the demasculinization of African clawed frogs when male frogs were exposed to less than 0.01 mg L^{-1} of atrazine (Hayes et al. 2002).

Organic materials used in denitrification walls and wood-chip bioreactors can act as a potential sorbent for the pesticides and veterinary antibiotics in the drainage water. Boudesocque et al. (2008) found that sorption of terbumeton, desethyl terbumeton, dimetomorph, and isoproturon by wood components and lignocellulosic materials was a fast process where less than 4 h was required to reach steady state, and the amount of pesticides sorbed by wood chips varied between 1 and 8 μg g^{-1}. Bras et al. (1999) found about 97% of heptachlor, aldrin, endrin, dieldrin, 1,1-dichloro-2,2-bis (*p*-chlorophenyl)ethane, 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane, and 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene were sorbed when 1 to 10 μg L^{-1} solutions of the pesticides were exposed to pine bark. Rodriguez-Cruz et al. (2007) investigated sorption of ionic and non-ionic pesticides onto hydrophilic (cellulose) and hydrophobic (lignin) wood components. The Freundlich distribution coefficient, K_f, for linuron ranged from 121 to 165 Lkg^{-1} for lignin and 2.2 Lkg^{-1} for cellulose indicating cellulose and lignin content of the wood residues affected their sorption potentials. Sharma et al. (2008) found that sawdust (42.3% carbon content), treated with 0.1 N H_2SO_4 and kept at 200°C for 4 h, removed about 74.7% to 80.5% of atrazine by sorption from a solution with starting concentrations of 0.05–0.1 mg L^{-1}. There are no studies on the sorption of antibiotics onto wood, but there are studies on the sorption of antibiotics onto soil particles.

Enrofloxacin, a fluoroquinolone carboxylic acid derivative, was strongly sorbed to various soil types with linear sorption coefficients (K_d) ranging between 260 and 5,612 Lkg^{-1} (Nowara et al. 1997). On the other hand, sulfamethazine, a sulfanomide, was found to be mobile in the soil due to its weak sorption (0.9–1.8 Lkg^{-1}) onto soil particles (Boxall et al. 2002). Sulfamethazine sorption onto soils increased with higher organic carbon contents and lower pH (Lertpaitoonpan et al. 2009). The organic carbon sorption coefficients (K_{oc}) of monensin A, an ionophore, for sorption onto soils were found to range from 2.1 and 3.8 Lkg^{-1} (Sassman and Lee 2007). Likewise, sorption of atrazine, a typical co-contaminant with nitrate, onto soil was found to be proportional to soil organic carbon content (Moorman et al. 2001).

There are currently no studies on the fate of pesticides, herbicides, and veterinary antibiotics in wood chip bioreactors or denitrification walls. The primary objective of this study was to investigate the sorption and desorption of herbicides and veterinary antibiotics onto wood chips obtained from a denitrification wall designed to treat nitrate in ground water entering a drainage tile. For the study, atrazine, sulfamethazine,

enrofloxacin, and monensin A were selected as representative chemicals of the main grouping of compounds: triazines, sulfonamides, fluoroquinolones, and ionophores, respectively. For comparison purposes, sorption studies were conducted using soils from the same field as the wood chip bioreactor. The effect of wood chips particle sizes on atrazine sorption was also evaluated.

2 Materials and Methods

2.1 Chemicals

Enrofloxacin (CAS number 93106-60-6, 99% purity), monensin sodium salt (CAS number 22373-78-0, 99% purity), and sulfamethazine (4-amino-*N*-(4, 6-dimethyl-2-pyrimidinyl)-benzenesulfonamide, CAS number 57-68-1, 99% purity) were purchased from Sigma-Aldrich (St. Louis, MO, USA) while atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) (CAS number 1912-24-9, 99% purity) was purchased from Chem Service (West Chester, PA, USA). Physical and chemical properties of the four compounds are enrofloxacin ($C_{19}H_{22}FN_3O_3$, molecular weight (M_W)=359.40, water solubility (solub.)=400 mg L^{-1}, p*K*a=6.27, 8.3), sulfamethazine ($C_{12}H_{14}N_4O_2S$, M_W= 278.33, solub. = 1500, p*K*a=2.65, 7.65), atrazine ($C_8H_{14}ClN_5$, M_W=215.69, solub. = 28, p*K*a=1.7), and monensin sodium salt ($C_{36}H_{61}NaO_{11}$, M_W= 692.9, solub. = 4.8–8.9, p*K*a=10.30) (Lizondo et al. 1997; Hoogerheide and Popov 1979; Tolls 2001). Stock solutions of enrofloxacin (1,000 mg L^{-1}) and atrazine (1,000 mg L^{-1}) were prepared in analytical grade acetonitrile. Monensin sodium salt stock solution of 100 mg L^{-1} was prepared in analytical grade methanol, and a sulfamethazine stock solution of 100 mg L^{-1} was prepared in high-performance liquid chromatography (HPLC) grade water. All standards for HPLC and liquid chromatography–mass spectrometry (LC–MS) calibration curves were prepared by diluting stock solutions in 10 mM $CaCl_2$ and stored at 4°C under dark conditions.

2.2 Sorbents

Wood chips for the sorption studies were collected at a depth of 170 cm from denitrification walls placed on both sides of a drainage tile in a field cropped with corn and soybean at Iowa State University agricultural research farm in Ames, Iowa (Jaynes et al. 2008). The wood chips had been in the denitrification walls for 5 years. The collected wood chips were air-dried and kept in a sealed bag at 4°C until they were used. The wood chips used for the denitrification wall were mainly oak (*Quercus* sp.) containing 46.54% organic C and 0.15% N. Over the 5 years, the field was not treated with manure or pesticides. Before the wood chips were used for the sorption experiments, the wood chips with a length or width larger than 5 cm were mechanically chopped with a blender to a size of less than 2 cm in width or length.

In addition to the wood chips, soil samples were collected from the same site at depths of 0–15, 80, and 168 cm. The soil samples from each depth were sieved through a 2-mm sieve, mixed, and stored in plastic bags at 4°C until they were used. Selected physical and chemical properties of the soil samples are presented in Table 1. The soil at this site is a Typic Endoaquoll in the Canisteo series.

2.3 Sorption and Desorption of Chemicals onto Woodchips and Soils

For each sorption isotherm experiment, a total of six 30-mL amber vials were used containing 1–2 g of wood chips in each vial. The wood chips were initially soaked in 10 mM $CaCl_2$ solution for 168 h to saturate the internal wood pore space. The solution was then drained and fresh $CaCl_2$ solution with 5,000 mg L^{-1} of sodium azide (NaN_3) added along with the chemical of interest for the sorption experiment. The initial concentrations of the four chemicals in the vials ranged from 0.5 to 8.0 mg L^{-1}. For each concentration, triplicate vials were prepared. The experiments were conducted at 22±1°C. After equilibration for 48 h, 2 mL of the supernatant was removed, filtered with 2-μm Whatman glass fiber filter, and analyzed using a HPLC. For the desorption experiments, a further 6 mL of the supernatant was removed from the tube and 8 mL of fresh 10 mM $CaCl_2$ solution added. The contents of the tubes were mixed for 48 h and then centrifuged. Two milliliters of supernatant was removed and filtered for HPLC analysis. The desorption procedure was repeated one more time.

Following the desorption experiments, the solutions in the tubes were drained, and 8 mL of 4:1 (*v*/*v*) mixture

Table 1 Selected physical–chemical properties of soils

Sample identification	Depth (cm)	Organic carbon (%)	pH	CEC (meq 100 g^{-1})	Sand (%)	Silt (%)	Clay (%)	Soil texture
Surface soil	0–15	2.15	7.7	23.1	37	36	27	Loam
Subsurface soil	80–120	0.64	7.6	12.7	57	23	20	Sandy clay loam
Subsurface soil	168	0.23	8.2	15.7	47	30	23	Loam

of acetonitrile–MilliQ water was added to the wood chips in the vials to extract atrazine, sulfamethazine or monensin A. The extraction pH was 6.3±0.7 for atrazine, 6.9±0.3 for sulfamethazine, and 6.8±0.4 for monensin A. The contents of the vials were mixed for 1 h with a reciprocating shaker and then equilibrated for 24 h. The vials were then centrifuged at 6,586×*g* for 20 min and the supernatants in the vials removed and saved. The wood chips were then extracted a second time using fresh 8 mL of the extraction solution. The supernatant of the second extraction was combined with the first extraction, and the acetonitrile in the combined extract (16 mL) of acetonitrile–water mixture was evaporated with nitrogen gas in an analytical evaporator. The concentrated supernatant was then cleaned and concentrated using Waters OASIS HLB cartridges as described below.

The mass of chemicals sorbed per unit mass of sorbent (milligrams per kilogram) was estimated based on the difference between the initial aqueous phase mass and equilibrium aqueous phase mass in the vial. The Freundlich distribution coefficients (K_f) and 95% confidence limits for the sorption–desorption isotherms were estimated by non-linear regression of the data to the Freundlich equation using SigmaPlot 10.0 software (Systat Software Inc., San Jose, CA, USA).

For soil samples, single-point sorption experiments were conducted. Three grams of soils (1 g of soil for enrofloxacin treatment) was placed into 30-mL FEP vials with 10 mL of 10 mM $CaCl_2$ solution and 1 mg L^{-1}atrazine, enrofloxacin, sulfamethazine, or monensin A. All vials also contained 5,000 mg L^{-1} of NaN_3 to inhibit microbial growth, except for the single-point sorption experiments with monensin A. The NaN_3 interfered with the LC–MS detection of monensin A. The sorption experiments were conducted twice and in triplicate. The contents of the vials were mixed for 48 h in a reciprocating shaker and then centrifuged at 6,574×*g* for 20 min. Two milliliters of the supernatant was removed and filtered through 2-μm Whatman glass fiber filter for HPLC analysis.

2.4 Effect of Wood Chip Particle Size on Sorption of Atrazine

Single-point sorption experiments were conducted to assess the effect of wood chip particle size on atrazine sorption. Wood chips were separated into three different sizes using 4 mm, 2 mm, and 150 μm sieves. An additional wood chips sample was obtained by mixing equal amounts by weight of the three sizes. Two grams of wood chips of each size was placed in 30 mL FEP vials along with 10 mL of 1.75 mg L^{-1} atrazine in 10 mM $CaCl_2$ solution and 5,000 mg L^{-1} NaN_3 after the wood chips were soaked in 10 mM $CaCl_2$ for 168 h. The sorption procedure was similar to that of the single-point sorption experiment for soils as described earlier. A separate single-point sorption experiment was conducted for the four wood chips sizes but without NaN_3 added. The linear sorption coefficients (K_d) were estimated based on mass sorbed and the equilibrium concentrations in the aqueous phases.

2.5 Sample Preparation and Chemical Analysis

The concentrated supernatants from the acetonitrile–MilliQ water extraction were cleaned and concentrated by passing the supernatant through the Waters OASIS HLB cartridges at a flow rate of approximately 0.5 mL min^{-1}. The flow rate for the conditioning or washing solution was 0.1 mL min^{-1}. Sample preparation for each chemical in the sorption–desorption experiments is presented below.

For atrazine analysis, the manufacturers' instructions were followed with a few modifications. The HLB cartridges were conditioned with 3 mL of 100% methanol (MeOH) followed by 3 mL of MilliQ water. The cartridges were then loaded with the

concentrated supernatant, and the cartridges washed with 3 mL of 5% MeOH in water followed by elution with 3 mL MeOH. Eluates were mixed with 3 mL of MilliQ water and the MeOH was evaporated, and the final volume was brought to 3 mL before the analysis with HPLC.

For sulfamethazine, the extraction steps followed the procedure developed by Henderson et al. (2009). For monensin A extraction, the method developed by Watanabe et al. (2008) was used with minor modifications. The cartridges were conditioned with 6 mL of MeOH followed by 6 mL of 0.5 N HCl and 6 mL of MilliQ water. After the concentrated supernatants were loaded through the cartridges, the cartridges were washed with 6 mL of MilliQ water loaded with 60 μL of 1.0 mg L^{-1} simeton as an internal standard. The cartridges were then eluted with 5 mL of MeOH. The MeOH in the extracts were evaporated and the volumes brought back to a volume of 1.2 mL by adding 500 μL of MeOH and 700 μL of MilliQ water. The extracts were then analyzed immediately with LC–MS.

For enrofloxacin, wood chips were extracted using a mixture of MeOH, ammonium acetate (10 mM), and MilliQ water in a ratio of 1:1:1 (*v*/*v*/*v*) with a pH of 6.3± 0.9. Extraction was conducted twice as for the other three chemicals. The enrofloxacin in the combined supernatant was concentrated and extracted using a method established by Gölet et al. (2001). The method was modified by using HLB cartridges instead of mixed phase cation exchange disk cartridges. The cartridge was conditioned with three-step procedure using 3 mL of MeOH, 3 mL of MilliQ, and 0.5 N HCl at pH 3 before the concentrated supernatant were loaded and the cartridges vacuum dried for 5 min. Enrofloxacin was eluted with 2.5 mL of 5% ammonium hydroxide in MeOH. The eluent was neutralized by adding 0.5 mL of 50 mM H_3PO_4 solution.

2.6 Chemical analysis

Atrazine and sulfamethazine were analyzed using an Agilent HPLC Series 1100 with diode array and enrofloxacin with a fluorescence detector. The HPLC eluent flow rate was set at 0.5 mL min^{-1} for atrazine and enrofloxacin analyses with the following solvents and times: 3 min with 10% acetonitrile and 90% HPLC grade water (4% glacial acetic acid and 1 mM ammonium acetate) followed by 70% acetonitrile and 30% water for 9 min and 10% acetonitrile and 90% water for the last 3 min. Retention times for atrazine and enrofloxacin were 12.1 and 8.1 min, respectively. The eluent flow rate for sulfamethazine was at 0.3 mL min^{-1} with 25% acetonitrile and 75% water for 8 min, increasing the acetonitrile to 45% for the next 3 min, followed by 100% acetonitrile for 2 min, and finally the acetonitrile reduced to 10% for last 5 min. Injection volumes were 20 μL for enrofloxacin, 30 μL for atrazine, and 50 μL for sulfamethazine. Detection wavelengths for atrazine and sulfamethazine were 254 nm. Excitation and emission wavelengths for fluorescence detection of enrofloxacin were 278 and 445 nm, respectively. HPLC column temperature was set at 60°C for atrazine and enrofloxacin and 40°C for sulfamethazine. Quantification was performed using external standards. Recovery of enrofloxacin freshly added to wood averaged 99%.

Monensin A was analyzed with a LC–MS equipped with SBC-18 Zorbax, Agilent column (2.1×150 mm with 3.5-μm particle size) based on the method developed by Watanabe et al. (2008) with modifications. The gradient was 30% water (HPLC grade water containing 5% acetonitrile and 0.1% formic acid) and 70% acetonitrile for 5 min followed by 5% water and 95% acetonitrile for 12.5 min and 30% water and 70% acetonitrile for 2 min. The sample volume used was 5 μL. Quantification was based on external standards using the monensin sodium adduct. Results are reported as monensin A. Detection limits for the four chemicals were atrazine 0.01 mg L^{-1}, enrofloxacin 0.005 mg L^{-1}, sulfamethazine 0.01 mg L^{-1}, and monensin A 0.001 mg L^{-1}.

3 Results and Discussion

3.1 Sorption Experiments

Sorption–desorption isotherms for all four chemicals are shown in Fig. 1. The Freundlich distribution coefficients, K_f, and linearity constants, n, along with their 95% confidence intervals for sorption and desorption of atrazine, sulfamethazine, enrofloxacin, and monensin A onto wood chips were determined by non-linear regression analysis. Results of the non-linear regression analysis are presented in Table 2. At the same time, the linear isotherm partition coefficients, K_d, were also estimated and reported in Table 2. The r^2 values for

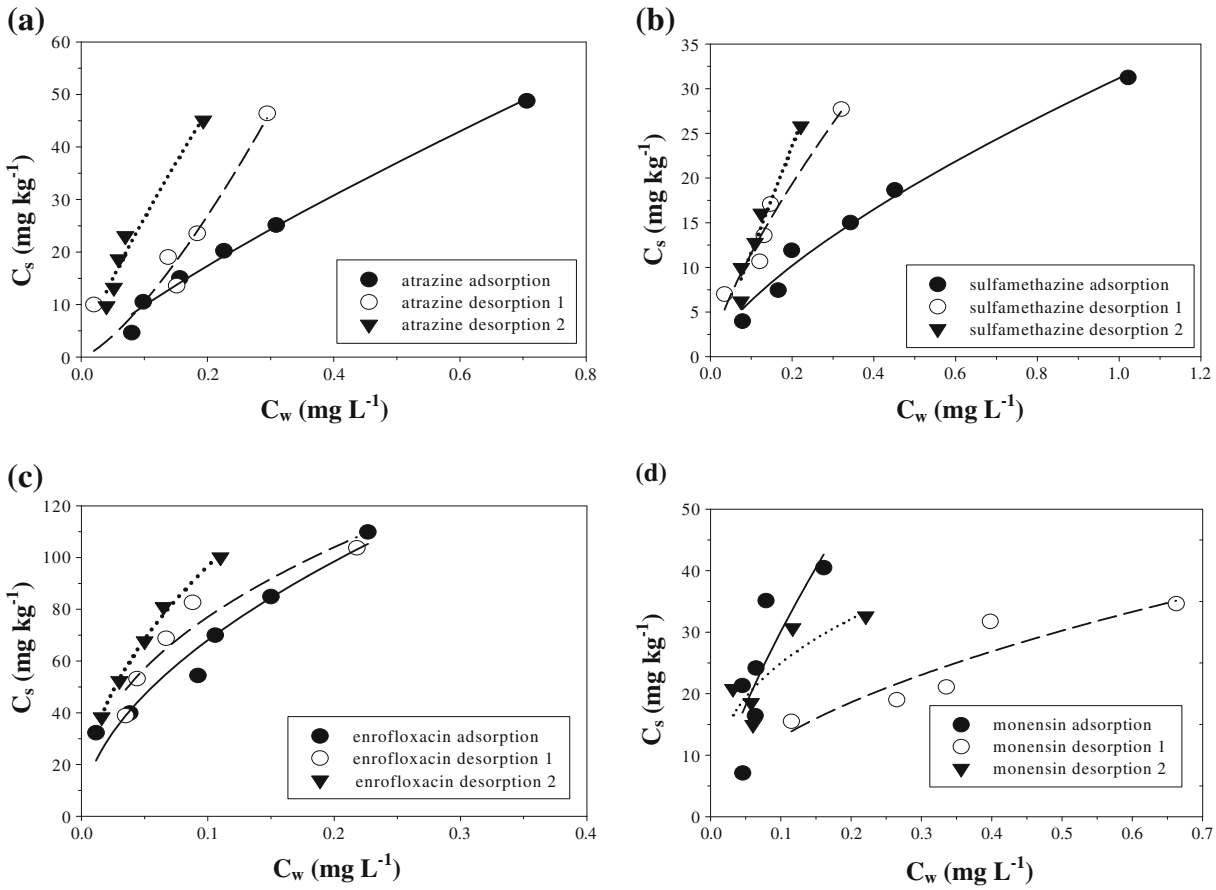

Fig. 1 Sorption–desorption isotherms of **a** atrazine, **b** sulfamethazine, **c** enrofloxacin, and **d** monensin A to wood chips. *Symbols* represent measured values (means, n=3). *Solid lines* show the isotherm predicted by non-linear regression using the Freundlich model

Freundlich isotherm were comparable to that of the linear isotherm. The n values for the Freundlich sorption isotherms were equal or lower than 0.82. According to Pignatello et al. (2006), n constants for Freundlich isotherms in the range of 0.95 and 1.05 are presumed to be linear isotherms.

The K_f for atrazine partitioning to wood (Table 2) was similar to the sorption of atrazine onto plant

Table 2 Freundlich sorption parameters (K_f, n) and linear partition coefficients (K_d), describing atrazine, enrofloxacin, monensin, and sulfamethazine sorption to wood (±95% confidence limit)

Chemical	Adsorption						First desorption			Second desorption		
	K_f	n_{sorp}	r^2	K_d	r^2	K_{oc} [a]	K_{fdes1} [b]	n_{des1}	r^2	K_{fdes2}	n_{des2}	r^2
Atrazine	65.5 ± 6.5	0.82	0.98	66 ± 12	0.98	141	176 ± 246	0.82	0.96	240 ± 66	1.35	0.82
Sulfamethazine	36.4 ± 3.1	0.79	0.98	35.0 ± 7.9	0.98	75	64 ± 23	0.74	0.95	127 ± 56	1.02	0.95
Enrofloxacin	232 ± 77	0.53	0.98	372 ± 31	0.99	799	209 ± 75	0.43	0.89	305 ± 37	0.49	0.99
Monensin A	161 ± 191	0.73	0.66	226 ± 12	0.63	486	44 ± 13	0.53	0.83	58 ± 37	0.36	0.58

[a] Estimated using wood chips organic carbon content of 46.54%

[b] Desorption measurements 48 h after sorption or first desorption experiments

residues (cuticle) with K_f between 120.8 and 137.37 Lkg^{-1} (Chefetz et al. 2003), but was much greater than sorption onto sugarcane mulch with K_f and K_d of 20.3 and 17.22 Lkg^{-1}, respectively (Selim and Zhu 2005). However, the K_f for atrazine sorption onto wood chips in this study was lower than K_f estimated by Boudesocque et al. (2008) for terbumeton sorption onto lignocellulosic material (1,090 Lkg^{-1}). Sorption of linuron, alachlor, and metalaxyl onto cellulose ranged between 1.36 and 9.15 Lkg^{-1} (Rodriguez-Cruz et al. 2009) which were lower than K_f estimated for atrazine onto wood chips in this study.

The atrazine K_{oc} for wood chips in this study was in the range of the K_{oc}'s (between 44.1 and 644.0 Lkg^{-1}) estimated for atrazine onto various organic plant residues (dewaxed cuticle, nonsaponifiable residue, nonhydrolyzable residue) with organic carbon contents ranging from 42.55% to 61.99% (Chefetz et al. 2003). The K_f and K_d values for wood chips in this study were of the same magnitude as the K_f and K_d of 44.3 and 43.1 Lkg^{-1} for soil with high (38.3%) organic carbon (Park et al. 2004). Atrazine sorption coefficients on Iowa soils with different physical and chemical properties ranged from 3.8 to 5.1 Lkg^{-1} (Novak et al. 1997) which was lower than the sorption coefficients for woodchips (65.8 Lkg^{-1}). Aromatic carbon and carboxylic acid unit content of the material play a significant role in atrazine binding onto organic materials where aromatic carbon content increases hydrophobic interactions in atrazine binding and carboxylic acids enhance hydrogen bonding between atrazine and organic matter (Lima et al. 2010). Therefore, strong binding of atrazine onto woodchips can be attributed to abundance of carboxylic units and aromatic groups on the wood chips.

Atrazine K_d values for soils (see Table 3) were within the range of the partition coefficients (0.4–5.8 Lkg^{-1}) reported by Moorman et al. (2001) for Iowa soils with organic carbon contents ranging from 0.08–2.54%. Atrazine K_d for wood chips was more than one order of magnitude larger than that for soils samples from the three depths, but the normalized atrazine K_{oc} values for wood chips were lower than the K_{oc} values for the soils at the three depths. Ling et al. (2006) observed a positive correlation between K_d and soil organic matter content. On the other hand, Mackay and Gschwend (2000) suggested that for wood particles, K_d were poorly correlated to the organic C of the wood which most probably was due to the narrow range of carbon contents among woods.

The K_f for sulfamethazine was similar to the linear partition coefficient, K_d (see Table 3), with the K_d value of sulfamethazine between 4 and 60 times larger than the K_d for the three soils at pH 6.1±0.4 (Table 3). Lertpaitoonpan et al. (2009) suggested that partitioning of sulfamethazine below pH 7.4 (pKa_2 for sulfamethazine) may be due to hydrophobic sorption since sulfamethazine was in the unionized form. The K_d values for the soils in this study were similar to that of Boxall et al. (2002) and Lertpaitoonpan et al. (2009) who reported K_d values between 0.9–1.8 and 0.6–2.8 Lkg^{-1}, respectively. Sulfonamide sorption to organic matter is related to the presence of phenolic and carboxylic groups, N-heterocyclic compounds, and lignin decomposition products (Thiele-Bruhn et al. 2004) which are assumed to result in hydrogen bonding and van der Waals interactions. Sulfamethazine sorbed the least in comparison to other chemicals tested. Sulfamethazine has the highest water solubility (1,500 mg L^{-1}) which reflects the ionic nature of the compound and may explain the lower K_f value compared to the other three compounds.

As expected, enrofloxacin was more strongly sorbed to wood chips (Table 2) and soil (Table 3) as compared to atrazine and sulfamethazine as indicated by Picó and Andreu (2007). Sorption to organic matter by hydrophobic mechanism and formation of cation

Table 3 Adsorption partition coefficients (K_d±95% CI) and K_{oc} of atrazine, enrofloxacin, monensin A, and sulfamethazine onto soils

Soil depth (cm)	Atrazine		Sulfamethazine		Enrofloxacin		Monensin A	
	K_d	K_{oc}	K_d	K_{oc}	K_d	K_{oc}	K_d	K_{oc}
0–15	4.2±0.2	197	5.5±10.8	256	2,747±1936	127765	26±24	1233
80–120	2.2±0.5	344	9.8±3.8	587	<DL	N/D	N/D	N/D
168	0.8±0.2	354	0.6±0.3	262	1,357±602	59,003	101±14	43,965

<*DL* below detection limit, *N/D* not determined

bridges in soil are likely mechanisms to explain enrofloxacin sorption onto soils (Tolls 2001). Boxall et al. (2006) reported K_{oc} values of 15,800 Lkg^{-1} for enrofloxacin which is about 20 times larger than K_{oc} estimated for wood chips.

Enrofloxacin partition coefficients for soils (Table 3) ranged from 1,357 to 2,746 Lkg^{-1}, which were within the range of K_d values found in the literature. For loamy sand with 2.27% organic carbon content, the K_d was reported to be 970 Lkg^{-1} (Ötker-Uslu et al. 2008). For clay minerals, the K_d was between 260 and 5,610 Lkg^{-1} (Nowara et al. 1997). Sorption of enrofloxacin onto surface soils was found to be higher than that of wood chips with K_d for wood chips about one order of magnitude smaller than that for surface soils.

Monensin A partition coefficients (see Table 2) were in the same range as enrofloxacin which was expected due to the low water solubility and large molecular size of these two compounds. The environmental fate of monensin is poorly understood (Dolliver et al. 2008), especially its sorption behavior onto environmental media. Carlson and Mabury (2006) suggested that monensin is immobile in soils and ionophore–cation complexes are highly lipophilic (Hansen et al. 2009). As shown in our results, monensin A was more strongly sorbed to subsurface soils than surface soils and wood chips (see Table 3). Sassman and Lee (2007) reported the log K_{oc} values of monensin as 2.1 to 3.8, which corresponds to 125.8 to 6,309 Lkg^{-1}, which were greater than the K_{oc} for monensin A in this study. They also found that reducing the pH of the soil from 6.2 to 4.9 which were below the p*K*a of monensin A resulted in an increase in K_d from 6.6 to 19.3 Lkg^{-1}.

The sorption experiments indicate that chemicals with different molecular sizes and chemical properties partition differently onto woodchips. Lignin (hydrophobic) and cellulose (polar) content of the wood also control sorption of hydrophobic compounds onto wood (Mackay and Gschwend 2000). The overall sorption results indicate that wood chips are good sorbents and can reduce agrichemical concentrations in tile water.

3.2 Desorption Experiments

Desorption isotherms for atrazine, enrofloxacin, and sulfamethazine after two desorption steps with water are shown in Fig. 1a–c, respectively. Both atrazine and sulfamethazine showed prominent sorption–desorption hysteresis. The three compounds did not desorb readily, which were reflected by increase in K_{fdes1} and K_{fdes2} values after each desorption step. The high sorption K_f values and the lack of desorption indicates the lack of mobility and bioavailability of the compounds in the wood chip bioreactor which, in turn, may affect their degradation. Atrazine sorption–desorption onto various soils or organic residues is well documented (Moorman et al. 2001; Bhandari and Lesan 2003; Chefetz et al. 2004; Lima et al. 2010), but there is a lack of information on sorption–desorption hysteresis for sulfamethazine, enrofloxacin, and monensin A with soil matrices or wood. The few studies on similar compounds showed that sorption–desorption hysteresis were observed for sorption of ofloxacin and sulfadiazine onto soils (Drillia et al. 2005; Sukul et al. 2008).

The desorption behavior of monensin A was different from desorption behavior of the other three compounds where a lower K_{fdes1} value was obtained as compared to the K_f value (see Fig. 1d). However, the value of K_{fdes2} value was statistically similar to that of K_f. This lower K_{fdes1} value shows that the binding of monensin A to wood chips may be due to external surface binding. Monensin A is a larger molecule than the other three molecules tested, and the penetration of the molecule into the micropores and the wood fibers and sorption to the surfaces of the micropores may be limited. As such, for the first desorption, about 12% of sorbed monensin A was desorbed readily.

To assess the extent of desorption, the desorption apparent hysteresis index (AHI), defined as the ratio of n_{des}/n_{sorp} (Huang et al. 1998), was estimated for each compound and presented in Table 4. The n_{des} in the AHI were estimated differently from n_{des1} and n_{des2} values in Table 3. The n_{des} was estimated by using the Freundlich equation, but the data used were the equilibrium concentrations of the sorption, first and second desorption steps for each initial concentration. Large AHI values would indicate decreasing ability of a chemical to desorb from a matrix (Chefetz et al. 2004; Drori et al. 2005). In general, lower AHI values were observed for atrazine and enrofloxacin, which ranged from 0.043 to 0.09 and 0.064 to 0.179, respectively (Table 4) as compared to sulfamethazine where the AHI values were between 0.133 and 0.245 (neglecting the AHI for the low concentration of 0.9 mg L^{-1}). The initial concentrations of enrofloxacin and their AHI values were found to be correlated (r^2= 0.95), whereas the initial concentrations and AHI

Table 4 AHI values for atrazine, sulfamethazine, and enrofloxacin

Chemical	C_i (mg L^{-1})	$K_{fdes,AHI}$	n_{des}	r^2	AHI
Atrazine	5.64	49.9	0.060	1.0	0.073
	2.81	26.4	0.054	0.81	0.066
	2.30	21.8	0.059	0.87	0.072
	1.72	16.4	0.074	0.45	0.090
	1.17	11.3	0.035	0.45	0.043
Sulfamethazine	4.20	32.1	0.134	0.99	0.169
	2.30	20.5	0.106	0.92	0.133
	1.90	17.2	0.126	0.93	0.158
	1.40	16.4	0.195	0.99	0.245
	0.90	7.8	0.040	0.15	0.050
Enrofloxacin	7.80	123.4	0.095	0.66	0.179
	4.50	94.5	0.056	1.0	0.106
	3.80	77.2	0.043	0.99	0.081
	2.80	59.0	0.034	0.98	0.064
	2.00	44.4	0.036	0.70	0.068

$K_{fdes,AHI}$ Freundlich coefficient calculated based on adsorption and two desorption data points for each initial concentration C_i, n_{desorp} linearity parameter for desorption estimated by non-linear regression, *AHI* ratio of n_{desorp}/n_{sorp}

values for sulfamethazine and atrazine were not linearly correlated with r^2 of 0.06.

3.3 Effect of Wood Chips Particle Size on Atrazine Sorption

Single-point partition coefficients for atrazine and different wood chips sizes with and without added NaN_3 are presented in Table 5. The K_d values increased with decreasing wood chips size. The atrazine K_d value for wood chips smaller than 2× 2 mm (128.8 Lkg^{-1}) was significantly higher than the K_d for wood chips larger than 4×4 mm (64.1 Lkg^{-1}) (F=3.63, P<0.05) with an exposure time of 168 h. On the contrary, Mackay and Gschwend (2000) showed that K_d's for wood sticks (1×0.16×0.16 cm), shavings, and chips (1×2×0.16 cm) were similar, ranging from 11 to 13 Lkg^{-1}, when the exposure time for the sorption experiments was 33 h. The presence of NaN_3 (5,000 mg L^{-1}) did not interfere with the sorption of atrazine onto wood chips. The K_d for the mixture of the three sizes was similar to the smallest particle size fraction between 150 μm and 2 mm. This may be due to the larger surface area provided by the smaller size particle which may control the sorption.

3.4 Extraction of Sorbed Chemicals from Wood Chips

Percent recoveries of the chemicals extracted from the wood chips after sorption by water and solvent

Table 5 Atrazine partitioning coefficients, K_d, for various wood chip particle sizes and in medium with and without NaN_3

Medium	Particle size			
	≥4 mm	2–4 mm	150 μm–2 mm	Homogeneous mixture
10 mM $CaCl_2$	63±23	97±12	129±14	134±40
10 mM $CaCl_2$ and 5,000 mg L^{-1} NaN_3	73±39	N/D	133±48	N/D

K_d = mean of three replications ±95% confidence interval

N/D not determined

desorption steps are presented in Fig. 2. Included in Fig. 2 are the unextractable percentages which are assumed to be the difference between the initial mass and the mass extracted by water and solvents. The initial water desorption yielded the greatest amounts of chemicals. The amounts extracted from wood chips by solvent desorption ranged from 12.2% to 21.3% for atrazine, 10.6% to 15.4% for sulfamethazine, 0.05% to 2.4% for enrofloxacin, and 0.1% to 0.8% for monensin A. In comparison, extraction of atrazine from sugarcane mulch with 100% MeOH resulted in a recovery of 5.49% (Selim and Zhu 2005) which was lower than the extractable percentage of atrazine from wood chips in this study. However, total incubation time should be taken into account in evaluating the extractable portions of the chemicals. Lesan and Bhandari (2004) reported the amount of atrazine recovered with water extraction (log K_{fd}=0.516) within 1 h of exposure was significantly different than atrazine extracted after 84 days of exposure (log K_{fd}= 0.965). For this study, chemicals were extracted on the eighth day after addition of the chemicals. The processes resulting in the irreversible binding (non-extractable fraction) are not known. Since similar partitioning of chemicals onto the wood was observed with and without sodium azide (Table 5), biological processes were not responsible. Wood is a highly porous material and some chemical may have entered the interior of the wood chips and become resistant to extraction.

4 Conclusion

Linear sorption coefficients, K_d and K_{oc}, for the sorption of atrazine, sulfamethazine, and monensin A onto wood chips were found to be greater than that for soils and subsoils at the same site where the in situ wood chips denitrification wall was located, indicating that both chemicals have a strong tendency to be sorbed onto the wood chips of denitrification walls. The higher sorption of chemicals by wood chips as compared to soils may be attributed to higher organic C

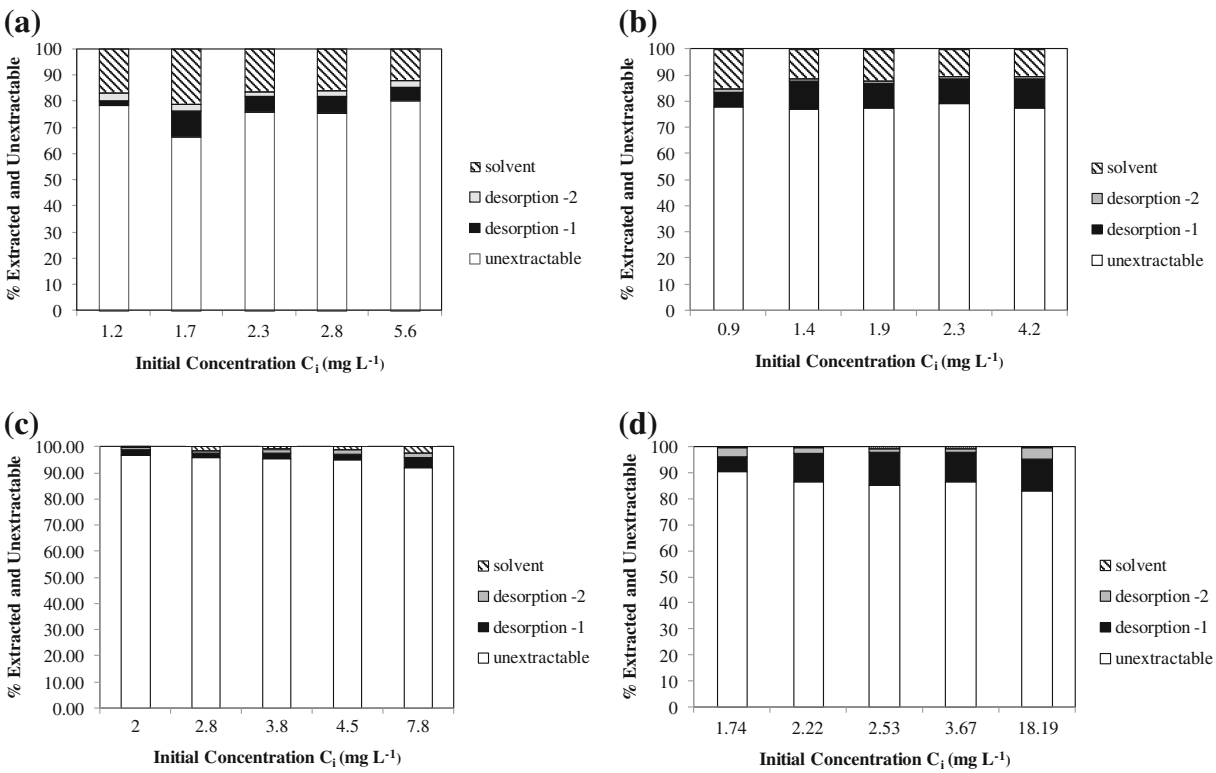

Fig. 2 Percent recoveries and unextractable for **a** atrazine, **b** sulfamethazine, **c** enrofloxacin, and **d** monensin A for sorption onto wood chips

content and the available macro- and micropores of the wood chips. On the other hand, sorption coefficients of enrofloxacin for soils were found to be about three orders of magnitude larger than the wood chips. Desorption hysteresis were observed for atrazine and sulfamethazine, and the estimated AHI values indicate that the chemicals were readily desorbed at higher initial concentrations as compared to lower initial concentrations. After two steps of desorption with water and solvent extraction, about 65% to 90% of the sorbed compounds remained on the wood. The results indicate that the chemicals were tightly bound to the wood chips and that the wood chips in denitrification walls or wood chips bioreactors can reduce the concentrations of atrazine, sulfamethazine, enrofloxacin, or monensin A present in tile drainage water. Since the primary purpose of the denitrification wall is to remove nitrate, the amount of woodchips used are significantly large and therefore under field conditions, these woodchips are not expected to reach the sorption saturation conditions of these chemicals. Of similar concern but not investigated in this study is the impact of the chemicals on the denitrification activity of the wood chips bioreactors.

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