Laboratory Evaluation of Zero Valent Iron and Sulfur–Modified Iron for Agricultural Drainage Water Treatment

by Barry J. Allred

Abstract

Agricultural subsurface drainage waters containing nutrients (nitrate/phosphate) and pesticides are discharged into neighboring streams and lakes, frequently producing adverse environmental impacts on local, regional, and national scales. On-site drainage water filter treatment systems can potentially prevent the release of agricultural contaminants into adjacent waterways. Zero valent iron (ZVI) and sulfur-modified iron (SMI) are two types of promising filter materials that could be used within these treatment systems. Therefore, water treatment capabilities of three ZVI and three SMI filter materials were evaluated in the laboratory. Laboratory evaluation included saturated falling-head hydraulic conductivity tests, contaminant removal batch tests, and saturated solute transport column experiments. The three ZVI and the three SMI filter materials, on average, all had a sufficient hydraulic conductivity greater than 1×10^{-3} cm/s. Batch test results showed a phosphate decrease of at least 94% for all tests conducted with the ZVI and SMI. Furthermore, the three SMI filter materials removed at least 86% of the batch test nitrate originally present, while batch tests for one of the ZVI filter materials exhibited an 88% decrease in the pesticide, atrazine. Saturated solute transport column experiments were carried on the best ZVI filter material, or the best SMI filter material, or both together, in order to better evaluate drainage water treatment effectiveness and efficiency. Results from these column tests additionally document the drainage water treatment ability of both ZVI and SMI to remove the phosphate, the ability of SMI to remove nitrate, and the ability of a select ZVI material to remove atrazine. Consequently, these findings support further investigation of ZVI and SMI subsurface drainage water treatment capabilities, particularly in regard to small- and large-scale field tests.

Introduction

Humid-region agricultural subsurface drainage practices commonly employ buried drainage pipe networks to remove excess soil moisture by lowering shallow water table levels, which in turn improves crop yields (Figure 1). Subsurface drainage is also utilized in semiarid to arid regions to prevent soil salinity build-up in farm fields. Agricultural fertilizer and pesticide application, combined with subsurface drainage practices, often produce adverse water quality impacts within the United States on local, regional, and national scales (Goolsby and Battaglin 2000; Myers et al. 2000; Sylvan et al. 2006; Scavia and Donnelly 2007; Alexander et al. 2008).

Nitrate (NO_3^-) is regarded as a major environmental concern with respect to subsurface drainage. Research conducted in the Midwest U.S. and Canada indicates that nitrate-nitrogen (NO_3^--N) concentration in waters discharged from agricultural subsurface drainage systems typically range from 0 to 50 mg/L, although higher values are certainly possible (Zucker and Brown 1998; Kalita et al. 2006; Kalita et al. 2007). Phosphate (PO_4^{3-}, also referred to as orthophosphate, dissolved phosphorus, or soluble reactive phosphorus) is another nutrient typically found in subsurface drainage waters. Past investigations indicate that subsurface drainage PO_4^{3-}-P values in production agricultural settings are generally less than 0.1 mg/L, but values occasionally above 1.0 mg/L have been reported (Kladivko et al. 1991; Sims et al. 1998; Kinley et al. 2007). Pesticides are also oftentimes present in agricultural drainage water (Kladivko et al. 1991; Dousset et al. 2004), and atrazine, used extensively for corn and sorghum production in the United States and Canada, happens to be one of the most common. Atrazine is usually found in subsurface drainage waters at relatively low concentrations, normally well less than 0.1 mg/L (Gaynor et al. 1995a; Kladivko et al. 1999; Yuan et al. 2000). However, Gaynor et al. (1995b) measured a maximum subsurface drainage water atrazine concentration of 0.35 mg/L in research conducted on small test plots.
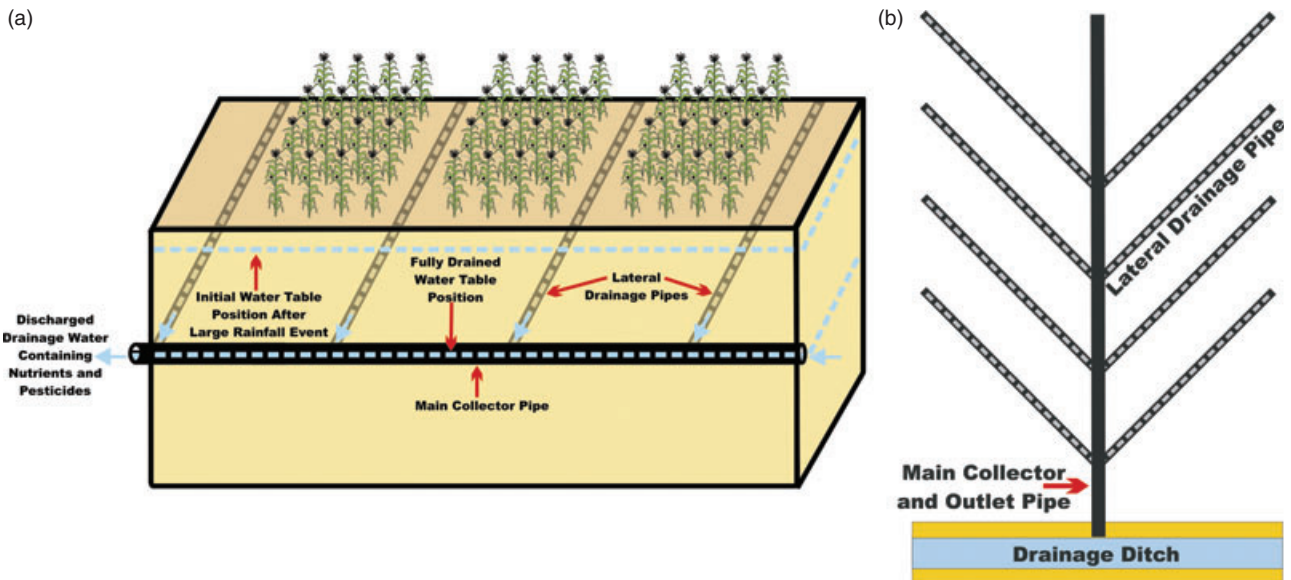
Figure 1. Typical subsurface drainage system: (a) buried drainage pipe network removes excess soil moisture by maintaining water table at or below pipe level and (b) plan view of common buried drainage pipe network pattern.

An in-line filter treatment system installed at a location along the pipe outlet of a typical subsurface drainage system (Figure 1) is potentially an attractive method for removing nutrients (e.g., NO_3^- or PO_4^{3-}) and pesticides from drainage waters before these waters are discharged into local waterways. As one design possibility, a trench backfilled with filter material, bottom-lined with impermeable clay or a geomembrane to prevent leaching, could be installed in-line on the pipe outlet to treat subsurface drainage waters from large agricultural fields. For a smaller subsurface drainage pipe systems, such as would be found on a golf course green, a filter cartridge of some form could be installed at the pipe outlet. Regardless of the filter treatment system design, the critical factor will be choosing the proper filter material that is efficient hydraulically and also effective with respect to contaminant removal.

Zero valent iron (ZVI) and sulfur-modified iron (SMI) are two promising filter materials that could be incorporated into a filter trench used to treat NO_3^-, PO_4^{3-}, and pesticides that are present in subsurface drainage waters. In the strictest sense, with respect to water treatment use, ZVI refers to powdered or granulated elemental iron materials having a valence state of zero. ZVI has been found to degrade NO_3^- to nitrogen gas (N_2) and ammonia/ammonium (NH_3/NH_4^+) by means of both biological and abiotic NO_3^- reduction (Choe et al. 2000; Westerhoff and James 2003; Biswas and Bose 2005). There are two possible mechanisms, by which ZVI can remove PO_4^{3-}. Iron oxidation processes can lead to the generation of ferrous/ferric iron (Fe^{2+}/Fe^{3+}) and the formation of iron oxide/hydroxide minerals (Drever 1982; Huang et al. 1998; Phillips et al. 2003; Henderson and Demond 2007). Ferrous and ferric iron can combine with PO_4^{3-} to form low solubility iron-phosphate precipitates (Stumm and Morgan 1981; Bohn et al. 1985). Alternatively, the iron oxide/hydroxide minerals that form have func-

tional groups sites where PO_4^{3-} could become attached via ligand exchange (Drever 1982; Bohn et al. 1985; McBride 1994). Chloro-organic pesticides, such as atrazine, are degraded by ZVI via reductive dechlorination (Ghauch et al. 1999; Ghauch and Suptil 2000; Dombek et al. 2001; Dombek et al. 2004).

SMI is a relatively unknown industrial product recently developed as a filter material for water treatment. This material is a hydrogen reduced, high surface area iron powder (ZVI) that has been additionally modified through chemical reaction with pure sulfur to produce sulfur/iron compound surface coatings on the iron particles. Specifics of the processes used to produce SMI are proprietary. The mechanisms by which SMI removes NO_3^-, PO_4^{3-}, and pesticides from water are likely the same (although possibly more reactive in some cases) as those mechanisms by which ZVI removes NO_3^-, PO_4^{3-}, and pesticides.

As previously discussed, limited prior research indicates that ZVI, and by extension, SMI, both have promise for use in treating drainage waters. However, additional investigation is certainly warranted to more fully document the overall feasibility of employing ZVI and SMI as filter materials to remove mixed nutrients (NO_3^-/PO_4^{3-}) and pesticides (such as atrazine) that are typically present in waters discharged by agricultural subsurface drainage systems. Therefore, a rigorous laboratory investigation was undertaken to evaluate ZVI and SMI viability in this regard. Three different ZVI materials and three different SMI materials were tested. To properly evaluate the filter treatment feasibility of ZVI and/or SMI, laboratory testing employed saturated falling-head hydraulic conductivity tests, contaminant removal batch tests, and saturated solute transport column tests. The stated research objective was therefore to conduct a laboratory evaluation of ZVI and SMI filter materials with respect to hydraulic efficiency and agricultural nutrient/pesticide water treatment capabilities.

Test Materials

Filter Materials

The following list provides information on the three ZVI filter materials, and the three SMI filter materials that were tested in this investigation. The four-character notations used to designate the individual filter materials throughout this article are also included in this list along with the filter material sources.

1. ZVI1: *Zero Valent Iron #1*
   > Recycled Ground Iron Aggregate.
   > Product Code: CC-1190.
   > Manufacturer: Connelly – GPM Inc., Chicago, Illinois.
2. ZVI2: *Zero Valent Iron #2*
   > Description: High Reactivity Iron Powder.
   > Product Code: H200.
   > Manufacturer: HEPURE Technologies Inc., Wilmington, Delaware.
3. ZVI3: *Zero Valent Iron #3*
   > Hydrogen Reduced Iron Powder.
   > Small-Scale Laboratory Production Sample.
   > Manufacturer: North American Höganäs Inc., Hollsopple, Pennsylvania.
4. SMI1: *Sulfur Modified Iron #1*
   > Hydrogen Reduced Iron Powder Reacted with Sulfur.
   > Small-Scale Laboratory Production Sample.
   > Developer/Marketer: SMI_PS Inc., Walnut Creek, California.
5. SMI2: *Sulfur Modified Iron #2*
   > Hydrogen Reduced Iron Powder Reacted with Sulfur.
   > Small-Scale Laboratory Production Sample with Granules >0.15 mm.
   > Developer/Marketer: SMI_PS Inc., Walnut Creek, California.
6. SMI3: *Sulfur Modified Iron #3*
   > Hydrogen Reduced Iron Powder Reacted with Sulfur.

Large-Scale Factory Production Sample.
Developer/Marketer: SMI_PS Inc., Walnut Creek, California.

Properties of the tested ZVI and SMI filter materials are provided in Table 1. The pH, electrical conductivity (EC), and oxidation/reduction potential (ORP) were measured on 1:1 by weight slurry mixtures of filter material and deionized water. Table 1 shows that the pH of the three ZVI materials (8.84 to 9.99) were considerably higher than the pH of the three SMI materials (6.13 to 6.41). Conversely, with regard to measured EC, the values for the three ZVI materials (0.33 to 1.48 dS/m) were substantially lower than the values for the three SMI materials (9.30 to 11.94 dS/m). The ORP values for all ZVI and SMI materials are negative; however, the ORP values for ZVI1, SMI1, SMI2, and SMI3 are much more negative (−313, −354, −663, and −449 mV, respectively) than the ORP values for ZVI2 and ZVI3 (−78 and −27 mV, respectively). These ORP measurements indicate that the use of ZVI1, SMI1, SMI2, and SMI3 could potentially produce very low redox conditions within a filter treatment system environment. Using mechanical sieving methods (Wray 1986) and a particle size classification based on Perloff and Baron (1976), Table 1 shows, with the exception of ZVI2, that the other five ZVI and SMI materials were comprised primarily of medium sand size and fine sand size particles. The ZVI2 material had a much smaller average particle size, with about half the particles being fine sand sized and half the particles being silt/clay sized.

Test Solutions

Synthetic drainage water solutions were mixed for this investigation. The constituent amounts and properties of these aqueous test solutions are provided in Table 2. The notations used to designate the different test solutions throughout this article are also included in Table 2. The moderate contaminant concentration solution (M), the two high contaminant concentration solutions (H1 and H2), and the extremely high contaminant concentration solution (EH), as their names imply, had moderate, high, and extremely high

Table 1
Filter Material Properties[1]

Filter Material	pH[2]	EC[3] (dS/m)	ORP[4] (mV)	Course Sand Size (2.0–4.75 mm)	Medium Sand Size (0.43–2.0 mm)	Fine Sand Size (0.075–0.43 mm)	Silt/Clay Size (<0.075 mm)
				Particle Size Distribution % by wt			
ZVI1	9.99	1.18	−313	0.00	59.83	37.82	2.35
ZVI2	9.31	0.33	−78	0.00	0.00	47.98	52.02
ZVI3	8.84	1.48	−27	0.02	16.08	76.18	7.72
SMI1	6.41	9.30	−354	0.02	17.84	76.50	5.64
SMI2	6.13	9.63	−663	0.00	27.86	71.72	0.42
SMI3	6.26	11.94	−449	0.00	17.52	77.96	4.52

[1]Values of pH, EC, and ORP were obtained from 1:1 by weight slurry mixtures of filter material and deionized water at ambient laboratory temperatures of 20 to 25 °C.
[2]The pH was determined using a Checker pH meter (Hanna Instruments, Woonsocket, RI).
[3]EC is electrical conductivity measured using a Field Scout Soil & Water EC Meter (Spectrum Technologies Inc. Plainfield, IL).
[4]ORP is oxidation/reduction potential measured using an EcoSense pH100 Meter and an YSI Inc., 115-1 ORP Probe (YSI Inc., Yellow Springs, Ohio).

Table 2

Test Solution Constituents and Properties[1]

Solution (Notation)	Nitrate-N (as KNO₃) (mg/L)	Phosphate-P (as Na₂HPO₄) (mg/L)	Atrazine (mg/L)	CaSO₄ (mg/L)	KCl (mg/L)	pH	EC[2] (dS/m)	ORP[3] (mV)
Moderate contaminant concentration (M)	10 (72)	0.1 (0.46)	0.1	565	140	6.92	1.04	134
High contaminant concentration #1 (H1)	25 (180)	0.25 (1.15)	0.4	565	140	6.72	1.14	110
High contaminant concentration #2 (H2)	50 (360)	0.25 (1.15)	0.4	565	140	7.01	1.38	196
Extremely high contaminant concentration (EH)	100 (720)	1.0 (4.60)	0.5	565	140	6.65	1.76	149
0.01 mol/L Calcium sulfate (CaSu)	—	—	—	1361	—	7.03	1.30	193

[1]Values of test solution pH, EC, and ORP were obtained at ambient laboratory temperatures of 20 to 25 °C.
[2]EC is electrical conductivity.
[3]ORP is oxidation/reduction potential.

concentrations of nitrate (NO_3^-), phosphate (PO_4^{3-}), and atrazine, based on previously discussed past investigations of subsurface drainage water quality. The 565 mg/L calcium sulfate ($CaSO_4$) and 140 mg/L potassium chloride (KCl) were added to the M, H1, H2, and EH solutions so that the inorganic anions/cations (SO_4^{2-}, Cl^-, Ca^{2+}, and K^+) normally found in subsurface drainage water were included in these solutions. Furthermore, when the Na_2HPO_4 added to the M, H1, H2, and EH solutions dissolved, a small amount of sodium (Na^+), another cation commonly found in drainage waters, was introduced along with the PO_4^{3-}. The H2 solution was used for all contaminant removal batch tests. The M, H1, and EH solutions were used for saturated solute transport column tests. The 0.01 mole/L $CaSO_4$ solution (CaSu) was employed for the saturated falling-head hydraulic conductivity tests.

Table 2 shows that the five test solutions had pH values near neutral and a narrow range of ORP, from 110 to 196 mV. The EC of a solution is used to gauge the solution salinity, and hence, the amount of dissolved anions/cations present. The EC measured for the test solutions utilized in this study ranged from 1.04 to 1.76 dS/m. Allred et al. (2008) found an EC range of 1.29 to 3.28 dS/m for soil solution extracted by suction lysimeters installed at three northwest Ohio fields having subsurface drainage and clay textured soils. These field-measured soil-solution EC values (1.29 to 3.28 dS/m), which are generally similar in magnitude to the EC values of the test solutions used in this study (1.04 to 1.76 dS/m), probably represent the upper range of EC values for subsurface drainage waters under Midwest U.S. conditions. For some added perspective, agricultural subsurface drainage EC values can be substantially larger in locations with arid or semiarid climates, for example, up to 8 dS/m in the San Joaquin Valley, California (Wichelns et al. 2002) and 32 dS/m in New South Wales, Australia (Hornbuckle et al. 2007). Consequently, the total amounts of dissolved anions and cations present in the research test solutions are

not unrealistic or excessive considering the wide range of EC measured salinity found around the world for subsurface drainage discharge.

Experimental Procedures

Saturated Falling–Head Hydraulic Conductivity Tests

Saturated hydraulic conductivity is the porous media property governing the rate at which drainage water flows through a filter material (e.g., ZVI or SMI) under saturated conditions. To be practical for drainage water treatment use from a hydraulic standpoint, a filter material must have a sufficiently high saturated hydraulic conductivity, at least equal to and preferably greater than 1.0×10^{-3} cm/s, which is a stormwater sand filter design criteria (Claytor and Schueler 1996; Barr Engineering Company 2001; Blick et al. 2004). Standard falling-head hydraulic conductivity tests (Freeze and Cherry 1979; Todd 1980) were employed for saturated hydraulic conductivity measurement. Saturated falling-head hydraulic conductivity tests were carried out on the three ZVI materials and the three SMI materials at ambient laboratory temperatures ranging from 20 to 25 °C.

For each individual filter material, duplicate saturated falling-head hydraulic conductivity tests were conducted so as to make certain that results were repeatable. That is, hydraulic conductivity measurements were obtained from two separately packed columns for each individual filter material. Owing to the limited amount of sample filter material available, the hydraulic conductivity tests for ZVI2, ZVI3, SMI1, and SMI2 were carried out with packed filter material columns that were 7.4 cm in length. As there was ample ZVI1 and SMI3 on hand, the hydraulic conductivity tests for these two filter materials were conducted with packed columns that were 14.9 cm in length. In addition, the packed columns were 4.1 cm in diameter, and saturated with CaSu solution 24 h prior to hydraulic conductivity measurement.

Contaminant Removal Batch Tests

Contaminant removal batch tests were carried out for ZVI1, ZVI2, ZVI3, SMI1, SMI2, and SMI3 at ambient laboratory temperatures ranging from 20 to 25 °. Control batch tests without filter material, designated by the notation NFM (no filter material), were also carried out to quantify contaminant amounts adsorbed by the experimental apparatus. These contaminant removal batch tests were conducted to provide a preliminary assessment of the potential contaminant removal capabilities for the three ZVI materials and the three SMI materials, and in turn decide if further saturated solute transport column testing was warranted for any of the ZVI or SMI materials. The repeatability of results for nitrate/phosphate/atrazine removal was confirmed by conducting a set of six-batch test replicates for each filter material and also NFM. A seventh replicate batch test was additionally carried out for each filter material (and NFM) to measure the pH, EC, and ORP within the reaction vessel immediately after batch test completion.

In each filter material batch test, 5 g of filter material and 40 g of the high contaminant concentration solution #2, H2, (Table 2) were combined in a 50 mL Teflon-FEP (fluorinated ethylene propylene) centrifuge tube. The filter material and H2 solution were thoroughly mixed by placing the Nalgene Teflon-FEP centrifuge tube (Thermo Fisher Scientific, Rochester, New York) containing filter material and H2 solution on a laboratory rotator (Mini LabRoller Rotator, Labnet International, Inc., Woodbridge, NJ) operated at 20 rpm. Each batch was then stopped after 24 h of mixing. Procedures for the control batch tests (NFM) were the same, but only H2 solution (40 g), but no filter material, was added to the Teflon centrifuge tube.

Again, for those filter material batch tests used to determine pH, EC, and ORP conditions, the pH, EC, and ORP measurements were obtained immediately after test completion and directly from the Teflon centrifuge tube reaction vessel containing the filter material and solution mixture (or solution alone in the case of NFM). For batch tests in which NO_3^-, PO_4^{3-}, and atrazine were measured, the Teflon centrifuge tubes containing filter material and solution were centrifuged (Beckman Model TJ-6 Centrifuge, Beckman Coulter, Inc., Fullerton, California) at 2500 rpm (800 g) for 10 min in order to separate the filter material from the solution. Part of the solution, set aside for atrazine analysis, was decanted into a 15-mL glass centrifuge tube and centrifuged at 2500 rpm (800 g) for an additional 60 min, then decanted once more into a second 15-mL glass centrifuge tube to ensure that all filter material had been removed from contact with the solution. The remaining solution in the original Teflon centrifuge tube was used for the analysis of NO_3^- and PO_4^{3-}. This remaining solution was itself decanted into a 50 mL polypropylene centrifuge tube and centrifuged at 2500 rpm (800 g) for an additional 60 min, then decanted once more into a 40-mL glass vial, again to ensure that filter material had been removed from contact with solution. The rather rigorous process of separating the solution from the filter material was performed for the purpose of discontinuing chemical reactions between the filter material and test solution after the batch test had finished. For consistency purposes, the same solution separation procedures were employed after completion of the control batch tests (NFM), even though these batch tests were conducted with solution only and no filter material.

Batch test pH, EC, and ORP were measured with equipment previously described (Table 1). Solution NO_3^- and PO_4^{3-} levels were measured at batch test completion as nitrate-nitrogen (NO_3^--N) and phosphate-phosphorus (PO_4^{3-}-P), respectively. Nitrate-nitrogen was determined colorimetrically by a copperized-cadmium reduction method (Parsons et al. 1984) using a QuikChem 8000 Flow Injection Analysis System (Lachat Instruments, Milwaukee, Wisconsin). Phosphate-phosphorus was determined colorimetrically by an ascorbic acid reduction method (Parsons et al. 1984) using the QuikChem 8000 Flow Injection Analysis System (Lachat Instruments). Atrazine concentrations were determined by immunoassay methods (Herzog 1997) using a RaPID Assay Atrazine Test Kit and RPA-I Analyzer (spectrophotometer) (Strategic Diagnostic Inc., Newark, Delaware).

Saturated Solute Transport Column Tests

By allowing control of solution flux and the filter material to solution exposure time, saturated solute transport column tests can help better evaluate the likely contaminant (NO_3^-, PO_4^{3-}, and atrazine) removal behavior of ZVI and SMI filter materials within an actual drainage water filter treatment system. For these column tests, a continuously operated peristaltic pump (Model 3384, Control Company, Friendswood, TX or C/L Dual-Channel, Masterflex, Vernon Hills, IL) delivered the initial influent nutrient/pesticide contaminant solution to the bottom inlet of a vertically oriented stainless steel permeameter containing a packed filter material column. Filter material columns contained within the stainless steel permeameters had a diameter of 4.7 cm and a length of 15.0 cm, although in one case, a 7.5-cm column was employed, and in another, a 30-cm-length column was utilized. Effluent exiting the permeameter was collected over time in glass containers. Excepting a small amount of silicon tubing threaded through the peristaltic pump, chemically inert Teflon tubing was used to deliver the solution between the influent supply container, peristaltic pump, permeameter, and effluent sample container. Ambient laboratory temperatures during testing ranged from 20 to 25 °C.

The pH was measured for all effluent samples, and then these samples were analyzed for NO_3^--N, PO_4^{3-}-P, and/or atrazine to determine ZVI or SMI effectiveness for drainage water treatment. Depending on the column test conducted, one, two, or all three of the agricultural contaminants were analyzed. Prior to contaminant measurement using previously described chemical analysis methods, effluent samples were centrifuged to remove any ZVI or SMI present. To ensure that the initial solution entering the permeameter was at the proper contaminant concentration levels, periodic samples were taken from the glass container that supplied solution to the permeameter inlet, and these samples were then analyzed for NO_3^--N, PO_4^{3-}-P, and/or atrazine.

Table 3 provides information on the nine saturated solute transport column tests conducted during this study. Of these nine column tests, there were two control tests with empty permeameters (no filter material present, designated NFM),

Table 3

Saturated Solute Transport Column Test Information

Test Number	Filter Material and (Solution)	Column Dry Bulk Packing Density (g/cm³)	Column Pore Volume[1] (mL)	Average Flow Rate or (Flux) (mL/h) (mL/cm² h)	Exposure Time (h)	Effluent Amount in (L) and (Effluent Pore Volumes)
1	NFM[2] (EH)	—	—	47.7 (2.7)	—	6.8 (-)
2	NFM[2] (EH)	—	—	46.8 (2.7)	—	9.5 (-)
3	ZVI1 (EH)	2.94	152.7	49.4 (2.8)	3.09	7.7 (50.4)
4	SMI3 (EH)	2.21	164.7	48.0 (2.7)	3.43	6.5 (39.5)
5	SMI3 (EH)	2.25	162.9	66.3 (3.8)	2.46	8.9 (54.6)
6	SMI3 (EH)	2.24	163.3	48.9 (2.8)	3.34	33.7 (206.4)
7	SMI3 (M)	2.25	162.9	50.1 (2.9)	3.25	8.2 (50.3)
8	SMI3 (H1)	2.34	79.5	482.3 (27.6)	0.16	3.3 (41.5)
9	SMI3/ZVI1 (EH)	2.22/3.11	164.2/146.4	51.3 (2.9)	3.20/2.85	14.8 (90.1/101.1)

[1]Column pore volumes and in turn the effluent amounts reported in pore volumes were calculated on the basis of a laboratory measured specific gravity (Wray 1986) of 7.03 g/cm³ for ZVI1 and 5.93 g/cm³ for SMI3.
[2]NFM is the notation for "no filter material," and in this case, an empty column.

one test with ZVI1 only, five tests with SMI3 only, and one test with ZVI1 and SMI3 together in a two-stage column. All column tests were carried out with the extremely high contaminant concentration solution, EH, except column test 7 which used the moderate contaminant concentration solution, M, and column test 8 which used the high contaminant concentration solution #1, H1 (Table 2). The EH solution was utilized for the large majority of column tests so that a more rigorous assessment could be obtained for ZVI1 and SMI3 water treatment effectiveness and efficiency. As shown in Table 3, column packing densities were greater with ZVI1 than SMI3.

Column tests 1 through 7 and 9 had average flow rates between 46.8 and 66.3 mL/h (corresponding flux: 2.7 to 3.8 mL/cm² h). On the basis of these flow rates and pore volumes calculated for the filter material columns, the estimated filter material to solution exposure time for column tests 3 through 7 and 9 ranged from 2.46 to 3.43 h. Exposure times of this magnitude would not be unrealistic for a filter treatment trench designed to remove nutrients and/or pesticides present in drainage waters discharged from an agricultural field. Column test 8 had a much greater flow rate of 482.3 mL/h (corresponding flux: 27.6 mL/cm² h), and in turn, a much lower filter material to solution exposure time of only 0.16 h (~10 min.). The total effluent collected for column tests 1 through 9 was between 3.3 and 33.7 L, and for the tests 3 through 9, carried out with packed filter material columns, total effluent amounts converted to pore volumes ranged from 39.5 to 206.4.

Empty column tests 1 and 2 were conducted for baseline comparison purposes in order to quantify the amounts of NO_3^-, PO_4^{3-}, and atrazine adsorbed by the experimental apparatus during testing. Problems with the laboratory chemical analysis equipment prevented accurate measurement of NO_3^--N for column test 1. Consequently, once these problems had been addressed, a second empty column test (column test 2) was carried out and effluent NO_3^--N measured. A direct contrast and appraisal of ZVI1 and SMI3 effectiveness/efficiency as filter materials to treat NO_3^-, PO_4^{3-}, and atrazine in drainage waters were accomplished not only by comparing the results from column test 3 (packed with ZVI1) against the results obtained for column test 4 (packed with SMI3), but also by comparing the results from column tests 3 and 4 against those results obtained for column tests 1 and 2.

Column test 5 was conducted to determine the byproduct of the NO_3^- degradation caused by SMI3. For column test 5, ammonia/ammonium-nitrogen (NH_3/NH_4^+-N) was measured in the column effluent along with NO_3^--N. Column 5 NH_3/NH_4^+-N effluent concentrations were analyzed by an outside laboratory (Service Testing and Research Laboratory, Ohio State University, Wooster, OH) using micro-Kjeldahl distillation methods (Mulvaney 1996). Column test 6 was a long duration test carried out to better define the overall capabilities of SMI3 to remove NO_3^- and PO_4^{3-} from drainage water over extended time. Column test 6 also evaluated whether mixing and repacking of the SMI3 filter material could extend its water treatment

life. Column test 7 assessed the effectiveness and efficiency of SMI3 to remove NO_3^- and PO_4^{3-} when these agricultural contaminants are originally present in the lower concentrations likely to be more typical of subsurface drainage waters (NO_3^--N at 10 mg/L and PO_4^{3-}-P at 0.1 mg/L). Column test 8 evaluated the capabilities of SMI3 to remove NO_3^- and PO_4^{3-} from drainage water given a very short filter material to solution exposure time of approximately 10 min. The short exposure time for column test 8 was produced with a 482.3 mL/h flow rate and a short 7.5-cm filter material column. The last column test, column test number 9, used ZVI1 and SMI3 together in a two-stage column to determine if the combination of these two filter materials can remove all three contaminants, NO_3^-, PO_4^{3-}, and atrazine, from drainage water. The column employed for column test 9 was 30 cm long, with the first 15 cm packed with SMI3 and the second 15 cm packed with ZVI1.

Results and Discussion

Saturated Falling–Head Hydraulic Conductivity Tests

Saturated hydraulic conductivity measurements are provided in Table 4 for the ZVI and SMI filter materials. Filter material packing densities for the saturated falling-head hydraulic conductivity tests are also provided in Table 4. Packing densities ranged from 1.72 to 3.21 g/cm^3. With the exception of one of two tests for ZVI2, all other ZVI and SMI saturated hydraulic conductivity measurements were above the previously discussed 1.0×10^{-3} cm/s criterion. The lowest two-test average hydraulic conductivity (2.12×10^{-3} cm/s) exhibited by ZVI2 (still greater than 1.0×10^{-3} cm/s) is probably due in large part to ZVI2 having a much greater amount of silt/clay-sized particles than the rest of the filter materials. The highest average hydraulic conductivity was obtained with ZVI1 (1.61×10^{-2} cm/s) and is likely

the result, at least in part, of ZVI1 having a much greater amount of medium sand-sized particles than the other filter materials tested. Consequently, overall results for the saturated falling-head hydraulic conductivity tests generally indicate that ZVI and SMI have sufficient hydraulic conductivity for drainage water filter treatment use.

Contaminant Removal Batch Tests

Results from the contaminant removal batch tests are provided in Table 5. The pH at batch test completion was significantly higher for the ZVI materials than that for the SMI materials. Conversely, EC was marginally greater for the SMI batch tests than that for ZVI batch tests. Values for ORP were negative for all ZVI and SMI batch tests; however, the ORP values for SMI batch tests were much more negative on the whole than the ORP values for the ZVI batch tests. The NFM batch test pH and EC were similar to those of the SMI batch tests, but unlike the ZVI and SMI batch tests, the measured NFM batch test ORP had a positive value.

The nitrate-nitrogen (NO_3^--N), phosphate-phosphorus (PO_4^{3-}-P), and atrazine solution concentrations at the beginning of each batch test were 50, 0.25, and 0.4 mg/L, respectively. The NFM batch tests results in Table 5 show that experimental apparatus and procedures alone will reduce nitrate (NO_3^-), phosphate (PO_4^{3-}), and atrazine concentrations respectively by −0.3%, 8.3%, and 11.1% on average. Consequently, PO_4^{3-} and atrazine contaminant reductions due to experimental apparatus and procedures should be taken into account when interpreting ZVI and SMI batch test results.

Batch test results indicate that SMI filter materials exhibit strong potential for drainage water NO_3^- removal, while the potential for NO_3^- removal by ZVI seems to be surprisingly limited. On average, batch tests with the three SMI filter materials exhibited at least 86% NO_3^- removal, while the greatest average NO_3^- removal obtained with the three ZVI filter materials was <10%. The largest average NO_3^- removal of 94.7% was observed with the SMI3 batch tests. Substantially, negative SMI batch test ORP values (Table 5) are indicative of low redox conditions conducive for the reduction of NO_3^- to nitrogen gas (N_2) and/or ammonia/ammonium (NH_3/NH_4^+). Nitrate reduction by ZVI is most effective within low pH (≤ 4.0) environments (Huang et al. 1998; Chen et al. 2005), which may explain the poor NO_3^- removal performance observed for the three ZVI filter materials, as ZVI batch test pH values were well above 8.0 (Table 5).

Batch test results show that all the ZVI and SMI filter materials have potential to remove substantial amounts of PO_4^{3-} from agricultural subsurface drainage waters. On average, the ZVI and SMI batch tests exhibited at least 94% PO_4^{3-} removal. Removal of PO_4^{3-} by ZVI and SMI, as previously mentioned, is probably due to the formation of iron-phosphate precipitates or PO_4^{3-} attachment via ligand exchange at functional group sites on iron oxide/hydroxide minerals (Stumm and Morgan 1981; Drever 1982; Bohn et al. 1985; McBride 1994). After taking into account the amount of atrazine reduction due to experimental apparatus and procedures, there was only one filter material,

Table 4

Filter Material Hydraulic Conductivities and Associated Packing Densities

Filter Material	Test Number	Column Dry Bulk Packing Density (g/cm³)	Saturated Hydraulic Conductivity (cm/s)
ZVI1	1	2.66	1.47×10^{-2}
	2	2.63	1.74×10^{-2}
ZVI2	1	3.10	9.77×10^{-4}
	2	3.21	3.26×10^{-3}
ZVI3	1	1.74	1.22×10^{-2}
	2	1.72	9.92×10^{-3}
SMI1	1	2.04	5.46×10^{-3}
	2	2.12	5.43×10^{-3}
SMI2	1	1.88	1.33×10^{-2}
	2	1.96	1.35×10^{-2}
SMI3	1	2.13	1.04×10^{-2}
	2	2.13	9.63×10^{-3}

Table 5
Contaminant Removal Batch Test Results[1]

Filter Material	Final Test Conditions			Average % Nutrient/Pesticide Removal (Standard Deviation of % Nutrient/Pesticide Removal)		
	pH	EC[2] (dS/m)	ORP[3] (mV)	NO_3^--N	PO_4^{3-}-P	Atrazine
ZVI1	8.75	1.21	−242	9.8 (1.1)	95.0 (4.3)	87.8 (2.5)
ZVI2	8.70	1.21	−111	1.6 (0.3)	97.7 (3.0)	8.7 (6.6)
ZVI3	9.67	1.36	−77	6.7 (1.8)	99.3 (1.8)	−3.2 (5.4)
SMI1	6.89	1.47	−310	90.0 (1.6)	94.4 (0.6)	36.7 (2.5)
SMI2	7.33	1.37	−362	86.4 (1.6)	99.3 (0.3)	20.2 (4.3)
SMI3	7.82	1.49	−422	94.7 (1.2)	97.3 (1.5)	16.5 (8.7)
NFM[4]	6.85	1.42	178	−0.3 (1.2)	8.3 (9.3)	11.1 (12.7)

[1]Batch test duration was 24 h.
[2]EC is electrical conductivity.
[3]ORP is oxidation/reduction potential.
[4]NFM is the notation for "no filter material."

ZVI1, which was shown to remove atrazine substantially. The average ZVI1 batch test atrazine removal was 87.8%, and reductive dechlorination is the likely process by which ZVI1 degraded atrazine (Ghauch et al. 1999; Ghauch and Suptil 2000; Dombek et al. 2001; Dombek et al. 2004).

Saturated Solute Transport Column Tests

Two filter materials, ZVI1 and SMI3, were chosen for saturated solute transport column testing. Both ZVI1 and SMI3 had sufficiently high hydraulic conductivity. Batch test results showed ZVI1 to be best at removing atrazine, while SMI3 was best at removing NO_3^-. The batch test results further indicate that ZVI1 and SMI3 are both potentially capable of removing substantial amounts of PO_4^{3-}. As drainage water NO_3^- tends to be of greater environmental concern than drainage water atrazine, the saturated solute transport column tests therefore focused more on SMI3 than ZVI1.

Results for column tests 1, 2, 3, and 4, with average flow rates between 46.8 to 49.4 mL/h, are depicted in Figure 2. The EH solution was used for these four column tests (NO_3^--N, PO_4^{3-}-P, and atrazine levels of 100, 1.0, and 0.5 mg/L, respectively). Column tests 1 and 2 were conducted without filter material and were employed to determine the amount of NO_3^-, PO_4^{3-}, and atrazine removed from solution due to experimental apparatus and procedures. Column test 2 results indicate that experimental apparatus and procedures do not remove NO_3^- from solution to any significant extent (Figure 2a). Column test 1 results show that experimental apparatus and procedures remove approximately 25% of PO_4^{3-} from solution at the beginning of the test, but there is only 4% PO_4^{3-} removal by the end of the test (Figure 2b). Column test 1 results further indicate that there is a 0% to 30% atrazine loss from solution that can be attributed to experimental apparatus and procedures (Figure 2c). Effluent pH for column test 1 varied between 6.26 and 6.77 (Figure 2d).

Column test 3 results indicate that ZVI1 can remove 21% (test start) to 6% (test end) of original NO_3^- and essentially all of the remaining PO_4^{3-} and atrazine not accounted

for by the loss due to experimental apparatus and procedures (Figure 2a, 2b, and 2c). Effluent for ZVI1 column test 3 had a pH that ranged from 8.45 to 9.25 (Figure 2d). Column test 4 showed SMI3 to remove 100% (test start) to 77% (test end) of original NO_3^- and essentially all of the remaining PO_4^{3-} not accounted for by the loss due to experimental apparatus and procedures (Figure 2a and 2b). Column test 4 results additionally imply that SMI is not particularly effective in removing atrazine from solution, because the amount of atrazine removed with SMI3 present is only modestly greater than that the amount of atrazine removed during a empty column test 1 (Figure 2c). Effluent pH for SMI3 column test 4 began the test at 3.79 and ended the test at 8.85 (Figure 2d). Altogether, the results for column tests 1, 2, 3, and 4 clearly indicate that ZVI1 has substantial capability to remove PO_4^{3-} and atrazine, while SMI3 has substantial capability to remove NO_3^- and PO_4^{3-}.

Results from column test 5 carried out with SMI3 are depicted in Figure 3. The EH solution containing 100 mg/L NO_3^--N was used. Column test 5 was conducted to determine the by-product of NO_3^- degradation caused by SMI3. Effluent from column test 5 was analyzed for ammonia/ammonium-nitrogen (NH_3/NH_4^+-N) along with NO_3^--N. Figure 3a shows that 71% to 84% of the original NO_3^--N was converted to NH_3/NH_4^+-N. The column effluent pH was between 6.87 and 9.01 (Figure 3b), indicating that at this pH level substantially more NH_4^+ was produced than NH_3 (CASTion Corporation 2008). The combined percent of NO_3^--N and NH_3/NH_4^+-N together in the column effluent ranged from 76% to 94%, which implies that SMI3 may have reduced some of the original NO_3^- to another by-product, such as nitrogen gas (N_2). (Note: Gas bubbles were observed exiting the permeameter outlet during column test 5.) Low-cost, abundant, natural zeolite has been proven effective for removing NH_4^+ from water via cation exchange processes (Booker et al. 1996; Demir et al. 2002; Sepaskhah and Yousefi 2007). Therefore, a two-stage filter treatment system in which drainage water first flows through SMI (to
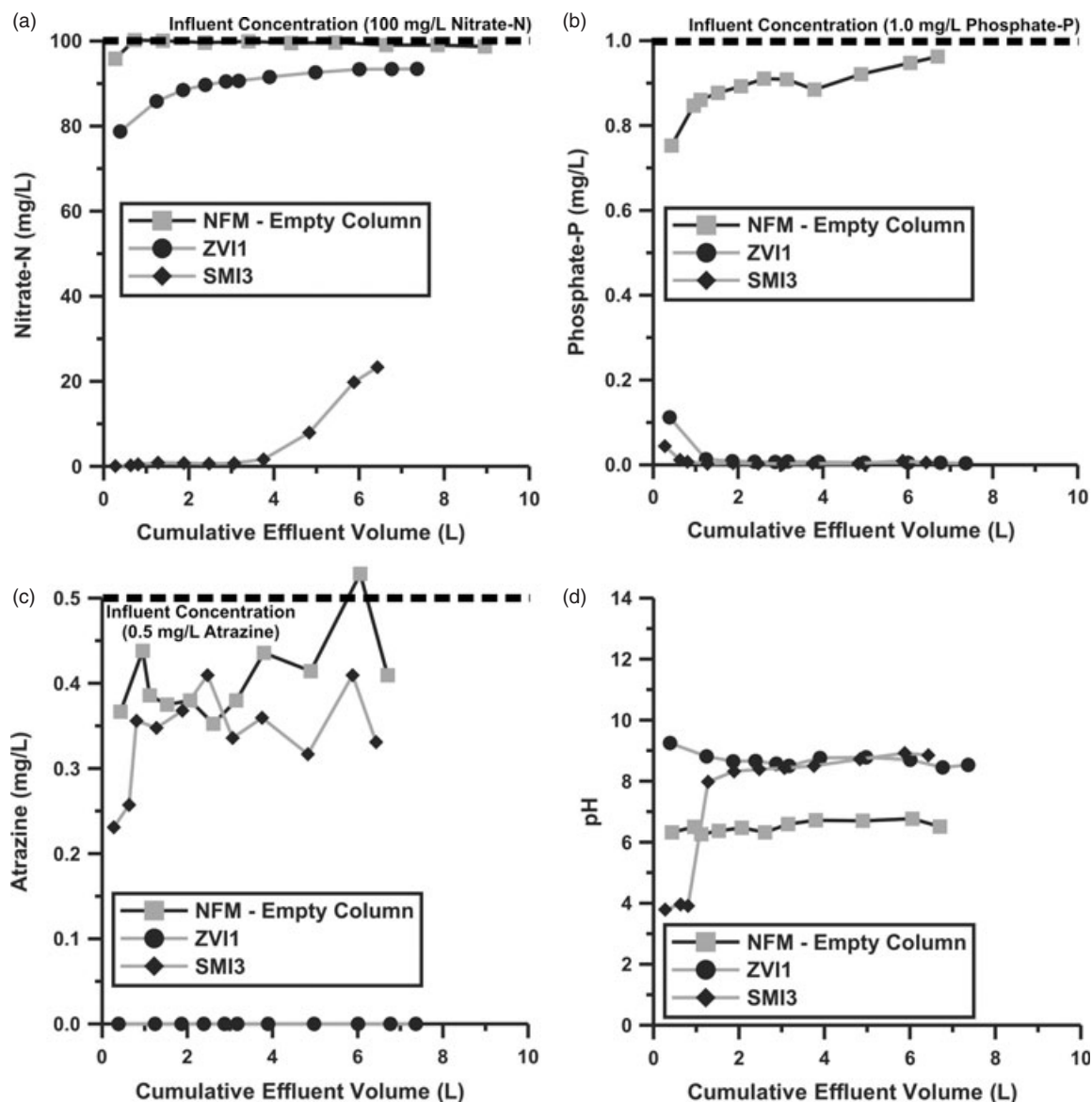
Figure 2. Results for saturated solute transport column tests 1 (NFM), 2 (NFM), 3 (ZVI1—50.4 total pore volumes of effluent and an exposure time of 3.09 h), and 4 (SMI3—39.5 total pore volumes of effluent and an exposure time of 3.43 h): (a) effluent NO_3^--N concentration, (b) effluent PO_4^{3-}-P concentration, (c) effluent atrazine concentration, and (d) effluent pH.

convert NO_3^- to NH_4^+) and then flows through zeolite (to remove the NH_4^+) could be a feasible way for taking out inorganic nitrogen originally present in subsurface drainage waters.

Results for column test 6 are presented in Figure 4. This column test was conducted with SMI3 and the EH solution. Column test 6 was a long duration test carried out to better define the overall capabilities of SMI3 to remove NO_3^- and PO_4^{3-} from drainage water over extended time. The average flow rate was 48.9 mL/h and effluent was collected over a 1-month period. The percent NO_3^- removal for column test 6 was 100% at the beginning, 60% after around 60 pore volumes (~10 L) of solution had been flushed, 40% after around 120 pore volumes (~20 L) of solution had been flushed, and by test end (206.4 pore volumes, 34 L), 10% NO_3^- removal was still being achieved (Figure 4a). More impressive, PO_4^{3-} removal was near 100% from beginning to end of the test (Figure 4b). Effluent pH was about 4.0 at

the beginning of the test, rose to a pH value of 8.85 after 12 pore volumes (~2 L) of solution been flushed, and remained within a pH range between 8.5 and 10.0 for the remainder of the test (Figure 4c). Consequently, over an extended period of time, SMI3 appears fairly capable of removing significant amounts of NO_3^- from drainage water, and extremely capable of removing PO_4^{3-} from drainage water.

Column test 6 also evaluated whether mixing and repacking of the SMI3 filter material could extend its water treatment life. The SMI3 column was mixed and repacked twice during this column test, the first time after approximately 120 pore volumes (~20 L) of effluent had been collected and the second time after approximately 180 pore volumes (~29 L) of effluent had been collected. Figure 4a shows that mixing and repacking of SMI3 produced dramatic improvements in NO_3^- removal that did not tend to last very long. Mixing and repacking of SMI3 did not seem to have much impact on PO_4^{3-} removal or effluent pH (Figure 4b and 4c).
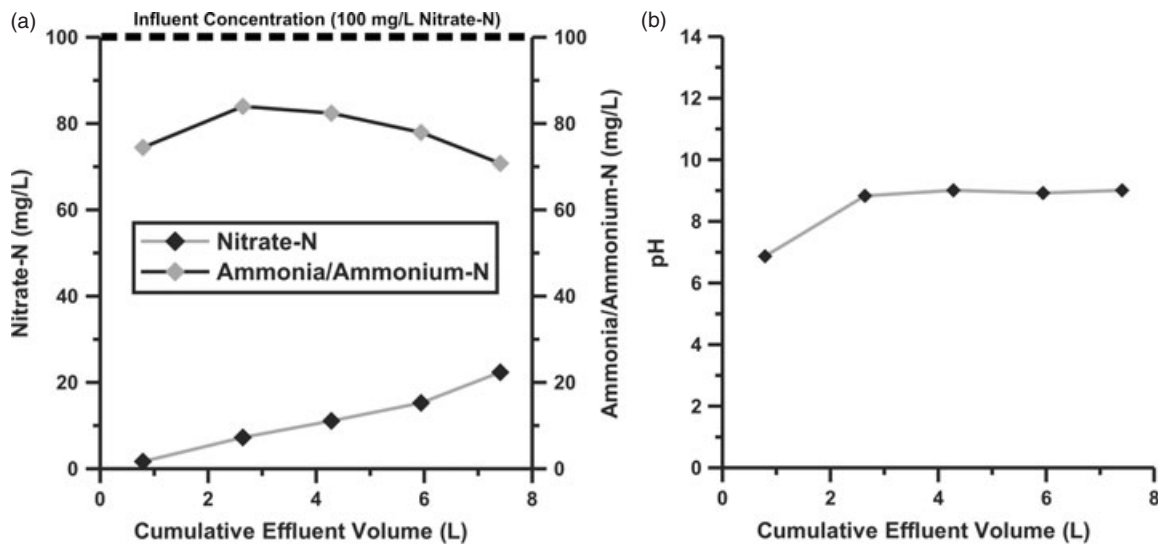
Figure 3. Results for saturated solute transport column test 5 with SMI3 having 54.6 total pore volumes of effluent and an exposure time of 2.46 h: (a) effluent NO$_3$$^-$-N and NH$_3$/NH$_4$$^+$-N concentration and (b) effluent pH.
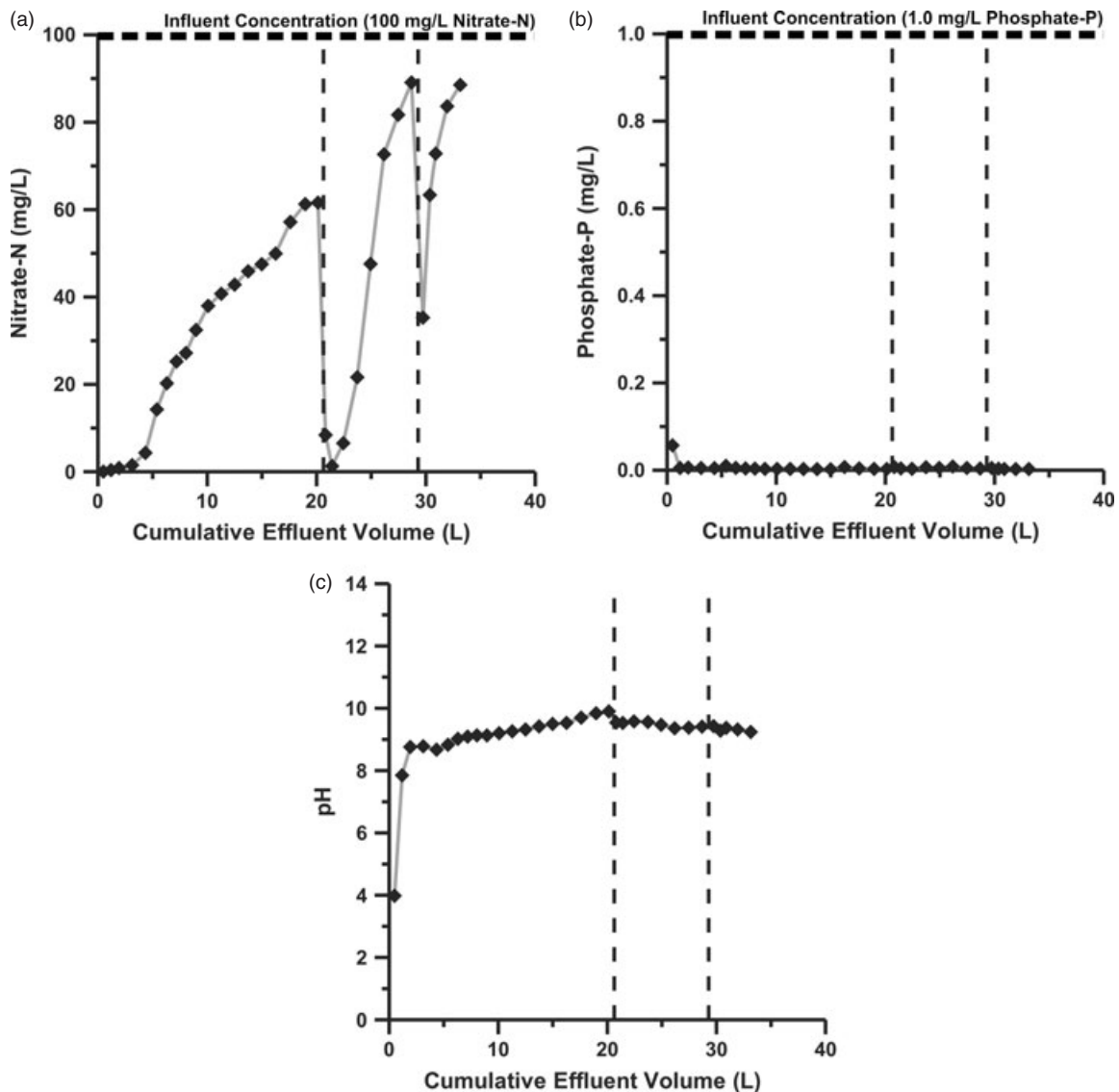

Figure 4. Results for saturated solute transport column test 6 with SMI3 having 206.4 total pore volumes of effluent and an exposure time of 3.34 h: (a) effluent NO$_3$$^-$-N concentration, (b) effluent PO$_4$$^{3-}$-P concentration, and (c) effluent pH. The dashed vertical lines reflect the two occasions during the test that the SMI3 material was mixed and then repacked into the permeameter.

Therefore, it is somewhat unclear whether there would be a substantial benefit to periodic mixing of SMI within an actual filter trench used to treat agricultural drainage waters.

The results for column test 7 can be found in Figure 5. The defined purpose of column test 7 was to assess the effectiveness and efficiency of SMI3 to remove NO_3^- and PO_4^{3-} when these agricultural contaminants are originally present in lower concentrations likely to be more typical of subsurface drainage waters. The moderate contaminant concentration solution, M, with NO_3^--N at 10 mg/L and PO_4^{3-}-P at 0.1 mg/L, was therefore employed to carry out column test 7. The percent NO_3^- removal was near 100% from beginning to the end of column test 7, in which 50 pore volumes of effluent were collected (Figure 5a). For comparison, column test 6 achieved 100% NO_3^- removal at the beginning of the test, which then reduced to 70% NO_3^- removal by the time 50 pore volumes of the EH solution (NO_3^--N at 100 mg/L) had been flushed through the column (Figure 4a). Consequently, the SMI3 water treatment life

regarding NO_3^- removal appears to increase as influent NO_3^- solution concentration decreases. Here, there is an implication that the SMI3 water treatment life for NO_3^- removal could be fairly long given more typical drainage water NO_3^- concentrations (around 10 mg/L NO_3^--N or less). Figure 5b shows that percent PO_4^{3-} removal was still quite good (80% to 95%) with lower influent PO_4^{3-}-P concentrations of 0.1 mg/L. Unlike the other SMI3 column tests, the effluent pH remained low (3.35 to 3.73) throughout the duration of column test 7 (Figure 5c).

The results for column test 8 are depicted in Figure 6. Column test 8 evaluated the potential of SMI3 to remove NO_3^- and PO_4^{3-} from drainage water given a very short filter material to solution exposure time of approximately 10 min (482.3 mL/h flow rate). The high contaminant concentration solution #1, H1, with NO_3^--N at 25 mg/L and PO_4^{3-}-P at 0.25 mg/L, was utilized to carry out this test. Even with a very short exposure time of 10 min, the percent NO_3^- removal at the beginning of the test was 100%, which
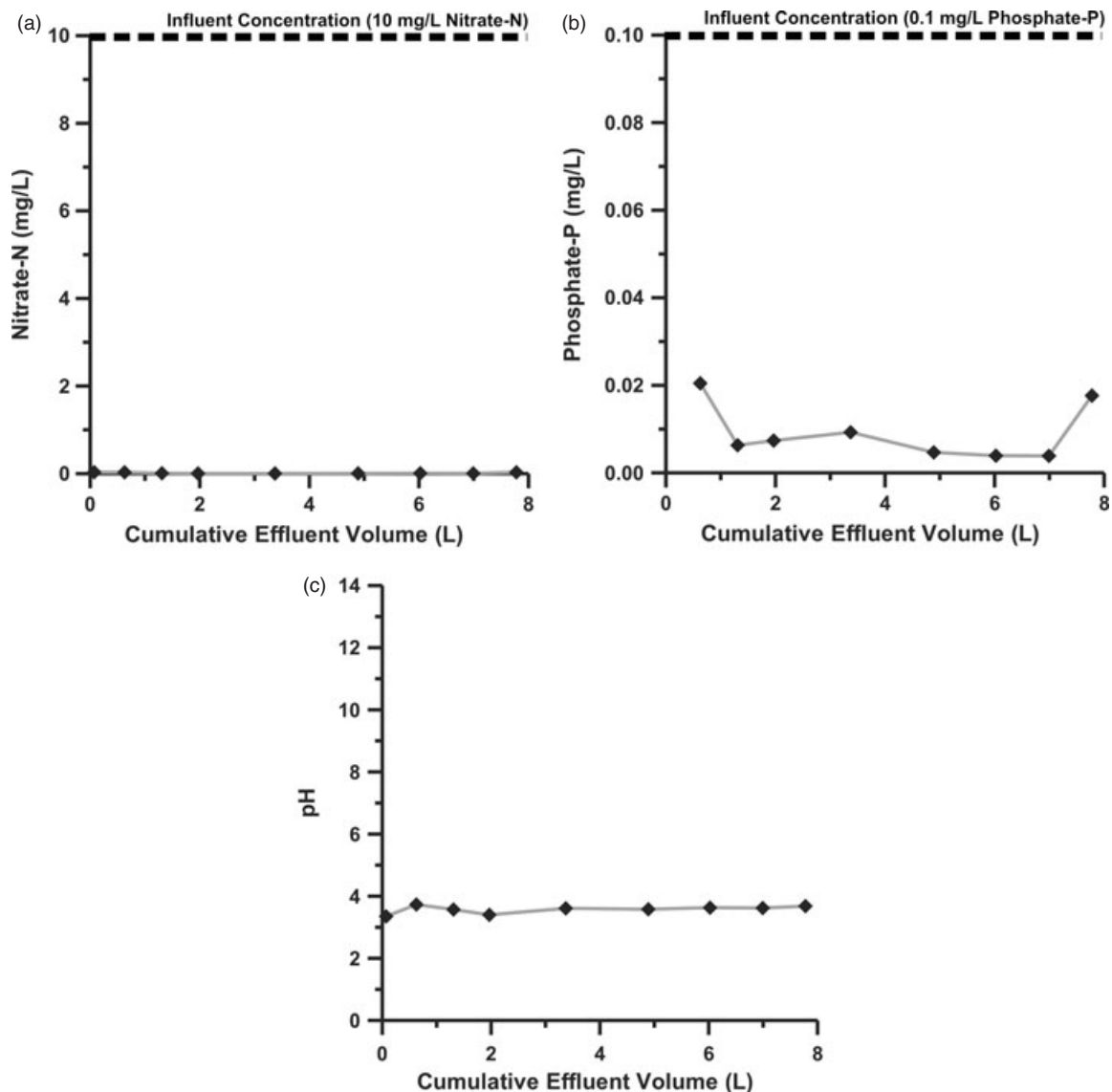
Figure 5. Results for saturated solute transport column test 7 with SMI3 having 50.3 total pore volumes of effluent and an exposure time of 3.25 h: (a) effluent NO_3^--N concentration, (b) effluent PO_4^{3-}-P concentration, and (c) effluent pH.
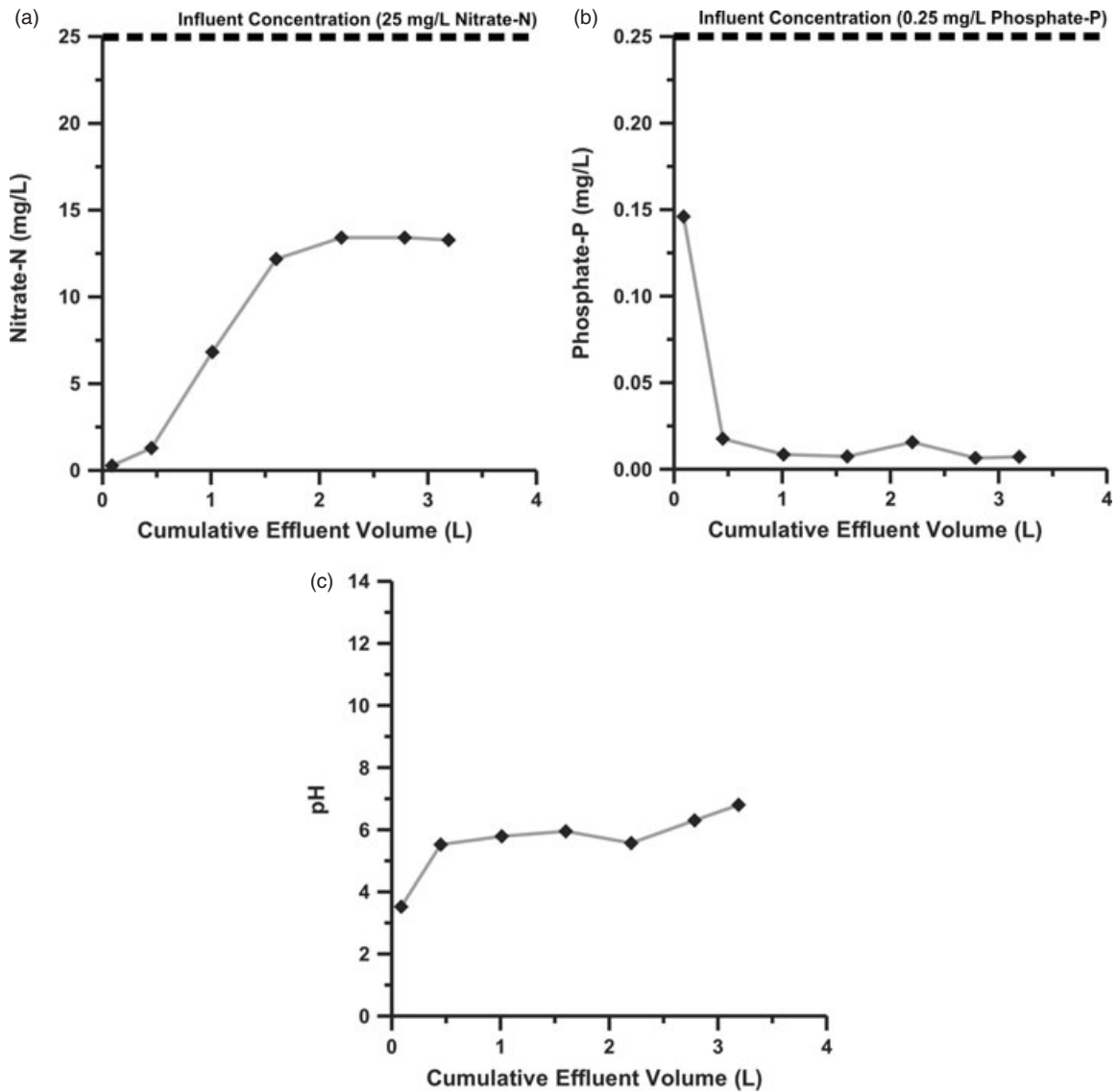
Figure 6. Results for saturated solute transport column test 8 with SMI3 having 41.5 total pore volumes of effluent and an exposure time of 0.16 h or 10 min: (a) effluent NO_3^--N concentration, (b) effluent PO_4^{3-}-P concentration, and (c) effluent pH.

then decreased to approximately 50% NO_3^- removal by test completion, after 40 pore volumes of flushing (Figure 6a). Perhaps more remarkable for column test 8 was that, with the exception of the initial effluent sample, at least 95% percent PO_4^{3-} removal was observed throughout the test (Figure 6b). Effluent pH was found to increase from 3.52 at the beginning of the test to 6.80 by the end of the test (Figure 6c). Consequently, the results from column test 8 clearly imply that SMI3 can remove substantial amounts of NO_3^- and PO_4^{3-} from agricultural subsurface drainage waters, even with a very short drainage water exposure time to the SMI3 filter material.

The results for column test 9 are provided in Figure 7. This last-saturated solute transport column test used ZVI1 and SMI3 together in a two-stage column to determine if the combination of these two filter materials could remove all three contaminants, NO_3^-, PO_4^{3-}, and atrazine, from drainage water. The EH solution (Table 2) was utilized to carry out this particular test. On the basis of the total amount of effluent collected (14.8 L), at least 90 pore volumes of solution were flushed through the first stage of the column containing SMI3, and 100 pore volumes of solution were flushed through the second stage of the column containing ZVI1. Figure 7a shows the percent NO_3^- removal at the beginning of column test 9 was 100%, which then decreased to approximately 50% NO_3^- removal by test completion. There was near 100% PO_4^{3-} removal from the beginning of the test to the end of the test (Figure 7b). For atrazine, there was 100% removal at the start of the test, and by test completion, atrazine removal was still greater than 90% (Figure 7c). Effluent pH remained within a narrow range of 8.73 to 9.14 throughout the test duration (Figure 7d). The effluent pH for column test 9 was in fact very similar to the magnitude and trend of effluent pH for column test 3 carried out with ZVI1 only. The overall results of column test 9 certainly indicate the potential for incorporating a select ZVI material and a select SMI material into separate compartments within an agricultural filter treatment system in
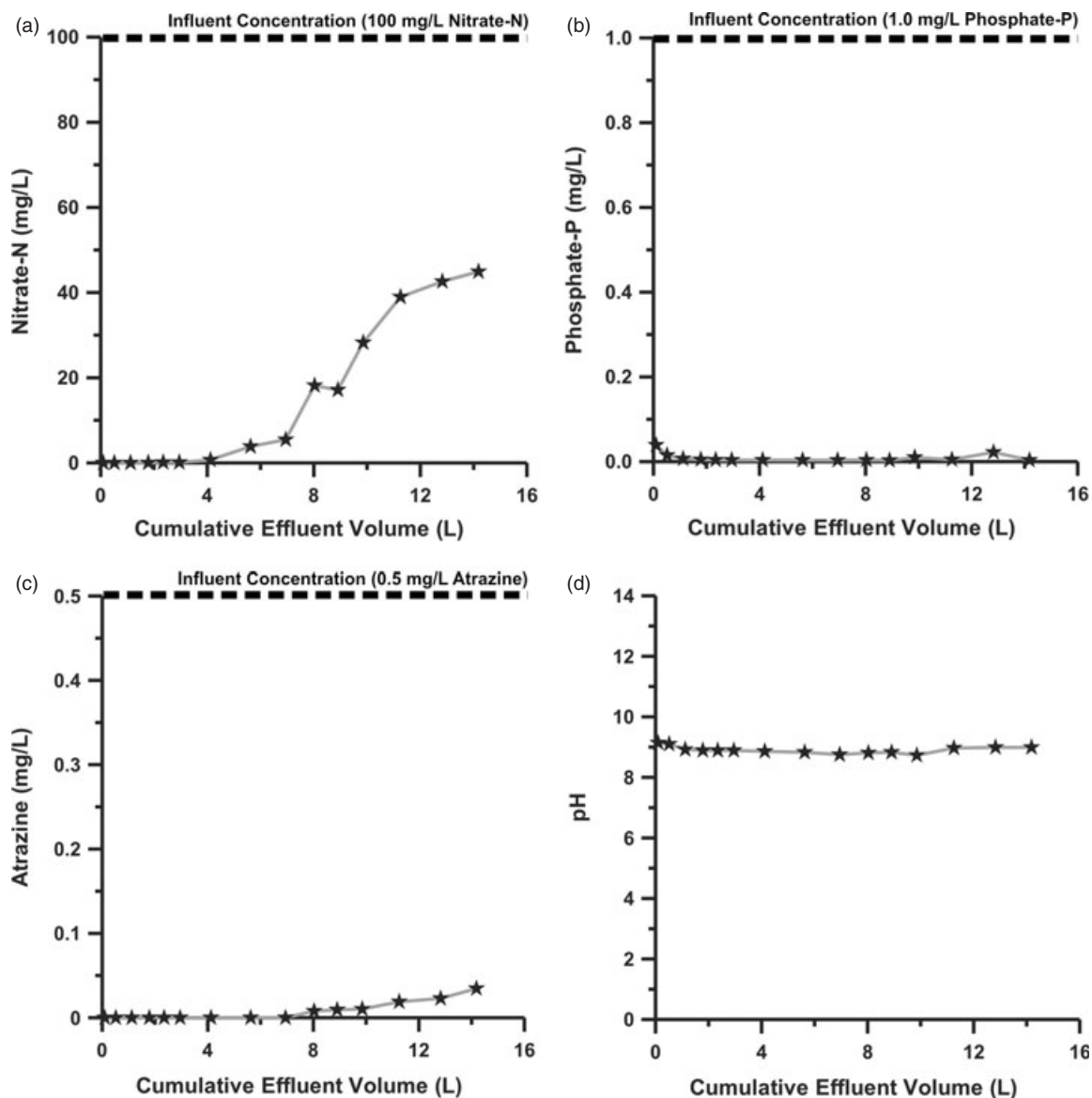
Figure 7. Results for saturated solute transport column test 9 with ZVI1 and SMI3 combined—90.1 total pore volumes of solution flushed through SMI3 1st stage, 101.1 pore volumes of solution flushed through ZVI1 2nd stage, SMI3 1st stage exposure time of 3.20 h, and ZVI1 2nd stage exposure time of 2.85 h: (a) effluent NO_3^--N concentration, (b) effluent PO_4^{3-}-P concentration, (c) effluent atrazine concentration, and (d) effluent pH.

order to remove not only nutrients, but also pesticides, from subsurface drainage waters.

Summary, Conclusions, and Future Work

The saturated falling-head hydraulic conductivity tests generally indicate that the ZVI and SMI filter materials have high enough hydraulic conductivities ($>1.0 \times 10^{-3}$ cm/s) to allow the sufficient water flow rates needed to make these filter materials hydraulically practical for use in drainage water filter treatment systems. Batch test results showed a PO_4^{3-} decrease of at least 94% for all tests conducted with the ZVI and SMI filter materials. Furthermore, the three SMI filter materials removed at least 86% of the NO_3^- originally present, while ZVI1 batch tests exhibited an 88% decrease in atrazine.

Column test results with the SMI3 filter material show that this specific SMI is potentially capable of removing substantial amounts of NO_3^- and PO_4^{3-} from drainage waters under conditions where initial levels of NO_3^- and PO_4^{3-} are moderate (nitrate-nitrogen, NO_3^--N, at 10 mg/L and phosphate-phosphorus, PO_4^{3-}-P, at 0.1 mg/L), where initial levels of NO_3^- and PO_4^{3-} are extremely high (NO_3^--N at 100 mg/L and PO_4^{3-}-P at 1.0 mg/L), over extended time periods, and in cases that the SMI filter material to drainage water exposure time is relatively short (~10 min). The by-product of NO_3^- reduction by SMI3 is predominantly ammonium (NH_4^+). Results of a column test with the ZVI1 material confirmed that this specific ZVI is capable of removing substantial amounts of PO_4^{3-} and atrazine. A column test with SMI3 and ZVI1 filter materials in series (first stage with SMI3—second stage with ZVI1) indicates that putting ZVI

and SMI together in a filter treatment system may possibly be a good approach for combined removal of NO_3^-, PO_4^{3-}, and pesticides, such as atrazine.

Consequently, these laboratory findings support further testing of ZVI and/or SMI for subsurface drainage water treatment. Perhaps most promising, ZVI and SMI appear to be especially good at reducing PO_4^{3-} levels in drainage waters. Before widespread adoption of ZVI and/or SMI for drainage water filter treatment can even be considered, both small-scale and large-scale field pilot tests need to be conducted over long periods of time with varying conditions (temperatures, contaminant concentrations, flow rates, intermittent saturation, etc.).

References

Alexander, R.B., R.A. Smith, G.E. Schwarz, E.W. Boyer, J.V. Nolan, and J.W. Brakebill. 2008. Differences in phosphorus and nitrogen delivery to the Gulf of Mexico from the Mississippi River Basin. *Environmental Science & Technology* 42: 822–830.

Allred, B.J., D. Groom, M.R. Ehsani, and J.J. Daniels. 2008. Resistivity methods. In *Handbook of Agricultural Geophysics*, ed. B.J. Allred, J.J. Daniels, and M.R. Ehsani, 85–108. Boca Raton: CRC Press.

Barr Engineering Company. 2001. *Minnesota Urban Small Sites BMP Manual*. St. Paul, Minnesota: Metropolitan Council Environmental Services.

Biswas, S., and P. Bose. 2005. Zero-valent iron-assissted autotrophic denitrification. *Journal of Environmental Engineering* 131: 1212–1220.

Blick, S.A., F. Kelly, J.J. Skupien, B. Friedman, S. Jacobus, G. McColligan, H. Birckhead, J. Morris, C. Obropta, P. Schiariti, K. Zomoradi, and C. Miller. 2004. *New Jersey Stormwater Best Management Practices Manual*. Trenton, New Jersey: New Jersey Department of Environmental Protection.

Bohn, H.L., B.L. McNeal, and G.A. O'Connor. 1985. *Soil Chemistry*, 2nd ed. New York: John Wiley & Sons.

Booker, N.A., E.L. Cooney, and A.J. Priestly. 1996. Ammonia removal from sewage using natural Australian zeolite. *Water Science and Technology* 34: 17–24.

CASTion Corporation. 2008. *Ammonia Removal in Municipal Sludge Dewatering Centrate: Pilot Test Results on Centrate*. Worcester, Massachusetts: CASTion Corporation.

Chen, Y., C. Li, and S. Chen. 2005. Fluidized zero valent iron bed reactor for nitrate removal. *Chemosphere* 59: 753–759.

Choe, S., Y. Chang, K. Hwang, and J. Khim. 2000. Kinetics of reductive denitrification by nanoscale zero-valent iron. *Chemosphere* 41: 1307–1311.

Claytor, R.A., and T.R. Schueler. 1996. *Design of Stormwater Filtering Systems*. Ellicott City, Maryland: The Center for Watershed Protection.

Demir, A., A. Gunay, and E. Debik. 2002. Ammonium removal from aqueous solution by ion-exchange using packed bed natural zeolite. *Water SA* 28: 329–335.

Drever, J.I. 1982. *The Geochemistry of Natural Waters*. Englewood Cliffs, New Jersey: Prentice-Hall, Inc.

Dombek, T.D., J. Davis, and D. Stine. Klarup. 2004. Degradation of terbutylazine (2-chloro-4-ethylamino-6-terbutylamino-1,3,5-triazine), deisopropyl atrazine (2-amino-4-chloro-6-ethylamino-1,3,5-triazine), and chlorinated dimethoxy triazine (2-chloro-4,6-dimethoxy-1,3,5-triazine) by zero valent iron and electrochemical reduction. *Environmental Pollution* 129: 267–275.

Dombek, T., E. Dolan, J. Schultz, and D. Klaruo. 2001. Rapid reductive dechlorination of atrazine by zero-valent iron under acid conditions. *Enviromental Pollution* 111: 21–27.

Dousset, S., M. Babut, F. Andreux, and M. Schiavon. 2004. Alachlor and bentazone losses from subsurface drainage of two soils. *Journal of Environmental Quality* 33: 294–301.

Freeze, R.A., and J.A. Cherry. 1979. *Groundwater*. Englewood Cliffs, New Jersey: Prentice-Hall, Inc.

Gaynor, J.D., D.C. MacTavish, and W.I. Findlay. 1995a. Atrazine and metolachor loss in surface and subsurface runoff from three tillage treatments in corn. *Journal of Environmental Quality* 24: 246–256.

Gaynor, J.D., C.S. Tan, C.F. Drury, I.J. Van Wesenbeeck, and T.W. Welacky. 1995b. Atrazine in surface and subsurface runoff as affected by cultural practices. *Water Quality Journal of Canada* 30: 513–531.

Ghauch, A., and J. Suptil. 2000. Remediation of s-triazines contaminated water in a laboratory scale apparatus using zero-valent iron powder. *Chemosphere* 41: 1835–1843.

Ghauch, A., J. Rima, C. Amine, and M. Martin-Bouyer. 1999. Rapid treatment of water contaminated with atrazine and parathion with zero-valent iron. *Chemosphere* 39: 1309–1315.

Goolsby, D.A., and W.A. Battaglin. 2000. Nitrogen in the Mississippi Basin – Estimating sources and predicting flux to the Gulf of Mexico. U.S. Geological Survey Fact Sheet 135-00. Reston, Virginia: USGS.

Henderson, A.D., and A.H. Demond. 2007. Long-term performance of zero-valent iron permeable reactive barriers: A critical review. *Environmental Engineering Science* 24, no. 4: 401–423.

Herzog, D.R. 1997. *Immunoassays for environmental contaminants: (Pesticides) in food and water. Technical Bulletin T00037*. Newark, Delaware: Strategic Diagnostics Inc.

Hornbuckle, J.W., E.W. Christen, and R.D. Faulkner. 2007. Evaluating a multi-level subsurface drainage for improved drainage water quality. *Agricultural Water Management* 89: 208–216.

Huang, C., H. Wang, and P. Chiu. 1998. Nitrate reduction by metallic iron. *Water Research* 32: 2257–2264.

Kalita, P.K., R.A. Cooke, S.M. Anderson, M.C. Hirschi, and J.K. Mitchell. 2007. Subsurface drainage and water quality: The Illinois experience. *Transactions of the ASABE* 50: 1651–1656.

Kalita, P.K., A.S. Algoazany, J.K. Mitchell, R.A.C. Cooke, and M.C. Hirschi. 2006. Subsurface water quality from a flat tile-drained watershed in Illinois U.S.A. *Agriculture, Ecosystems & Environment* 115: 183–193.

Kinley, R.D., R.J. Gordon, G.W. Stratton, G.T. Patterson, and J. Hoyle. 2007. Phosphorus losses through agricultural tile drainage in Nova Scotia, Canada. *Journal of Environmental Quality* 36: 469–477.

Kladivko, E.J., J. Grochulska, R.F. Turco, G.E. Van Scoyoc, and J.D. Eigel. 1999. Pesticide and nitrate transport into subsurface tile drains of different spacings. *Journal of Environmental Quality* 28: 997–1004.

Kladivko, E.J., G.E. Van Scoyoc, E.J. Monke, K.M. Oates, and W. Pask. 1991. Pesticide and nutrient movement into subsurface tile drains on a silt loam soil in Indiana. *Journal of Environmental Quality* 20: 264–270.

McBride, M.B. 1994. *Environmental Chemistry of Soils*. New York: Oxford University Press, Inc.

Mulvaney, R.L. 1996. Nitrogen – inorganic forms. In *Methods of Soil Analysis: Part 3 –Chemical Methods, Soil Science Society of America Book Series*, vol. 5, ed. D.L. Sparks, 1129–1139. Madison, Wisconsin: American Society of Agronomy and Soil Science Society of America.

Myers, D.N., M.A. Thomas, J.W. Frey, S.J. Rheaume, and D.T. Button. 2000. Water Quality in the Lake Erie – Lake Saint Clair Drainages: Michigan, Ohio, Indiana, New York, and

Pennsylvania, 1996–1998. U.S. Geological Survey Circular 1203. Denver, Colorado: USGS.

Parsons, T.R., Y. Maita, and C.M. Lalli. 1984. *A Manual of Chemical and Biological Methods for Seawater Analysis.* Oxford, UK: Pergamon Press.

Perloff, W.H., and W. Baron. 1976. *Soil Mechanics – Principles and Applications.* New York: John Wiley & Sons.

Phillips, D.H., B. Gu, D.B. Watson, and Y. Roh. 2003. Impact of sample preparation on mineralogical analysis of zero-valent iron reactive barrier materials. *Journal of Environmental Quality* 32: 1299–1305.

Scavia, D., and K.A. Donnelly. 2007. Reassessing hypoxia forecasts for the Gulf of Mexico. *Environmental Science & Technology* 41: 8111–8177.

Sepaskhah, A.R., and F. Yousefi. 2007. Effects of zeolite application on nitrate and ammonium retention of a loamy soil under saturated conditions. *Australian Journal of Soil Research* 45: 368–373.

Sims, J.T., R.R. Simard, and B.C. Joern. 1998. Phosphorus loss in agricultural drainage: Historical perspective and current research. *Journal of Environmental Quality* 27: 277–293.

Stumm, W., and J.J. Morgan. 1981. *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters,* 2nd ed., New York: John Wiley & Sons.

Sylvan, J.B., Q. Dortch, D.M. Nelson, A.F. Maier Brown, W. Morrison, and J.W. Ammerman. 2006. Phosphorus limits phytoplankton growth on the Louisiana Shelf during the period of hypoxia formation. *Environmental Science & Technology* 40: 7548–7553.

Todd, D.K. 1980. *Groundwater Hydrology,* 2nd ed. New York: John Wiley & Sons.

Westerhoff, P., and J. James. 2003. Nitrate removal in zero-valent iron packed columns. *Water Research* 37: 1818–1830.

Wichelns, D., D. Cone, and G. Stuhr. 2002. Evaluating the impact of irrigation and drainage policies on agricultural sustainability. *Irrigation and Drainage Systems* 16: 1–14.

Wray, W.K. 1986. *Measuring Engineering Properties of Soil.* Englewood Cliffs, New Jersey: Prentice-Hall, Inc.

Yuan, Y., J.K. Mitchell, S.E. Walker, M.C. Hirschi, and R.A.C. Cooke. 2000. Atrazine losses from corn fields in the Little Vermilion River Watershed in east central Illinois. *Applied Engineering in Agriculture* 16: 51–56.

Zucker, L.A., and L.C. Brown. 1998. Agricultural drainage: Water quality impacts and subsurface drainage studies in the Midwest. OSU Extension Bulletin 871. Columbus, Ohio: Ohio State University.

Biographical Sketch

Barry J. Allred, corresponding author, is a Research Agricultural Engineer with the USDA/ARS–Soil Drainage Research Unit, 590 Woody Hayes Drive, Room 234, Columbus, OH 43210; (614) 292-9806; fax: (614) 292-9448; Barry.Allred@ars.usda.gov.