Use of Industrial Byproducts to Filter Phosphorus and Pesticides in Golf Green Drainage Water

Sheela G. Agrawal,* Kevin W. King, James F. Moore, Phil Levison, and Jon McDonald

Golf courses are vulnerable to phosphate ($\text{PO}_4^{3-}$) and pesticide loss by infiltration of the sandy, porous grass rooting media used and through subsurface tile drainage. In this study, an effort was made to remove $\text{PO}_4^{3-}$, chlorothalonil, mefenoxam, and propiconazole in a golf green’s drainage water with a filter blend comprised of industrial byproducts, including granulated blast furnace slag, cement kiln dust, silica sand, coconut shell-activated carbon, and zeolite. To test this filter media, two 6-h storm events were simulated by repeat irrigation of the golf green after $\text{PO}_4^{3-}$ and pesticide application. Drainage flows ranged from 0.0034 to 0.6433 L s$^{-1}$ throughout the course of the simulations. A significant decrease in the chlorothalonil load for the experimental run (with filter media) was observed compared with the control (without filter media) ($p < 0.05$). In general, percent reductions in chlorothalonil were very high (>80%) near peak flows. In contrast, filter media was not effective in removing $\text{PO}_4^{3-}$, mefenoxam, or propiconazole ($p > 0.05$). Instead, it appears that the filter blend added $\text{PO}_4^{3-}$ to the effluent above flow rates of 0.037 L s$^{-1}$. Overall, flow rate, the amount of filter media used, and contaminant properties may have influenced the filter media’s ability to remove contaminants. More research is needed to determine the optimal blend and configuration for the filter media to remove significant amounts of all contaminants investigated.

There are over 50 million acres of turfgrass (parks, roadsides, private and commercial lawns, golf courses, cemeteries, sod farms, etc.) in the United States, of which golf courses comprise approximately 3.2% (King and Balogh, 2006). Despite their seemingly small land area percentage, golf courses can adversely affect surface water quality because of the frequent applications of fertilizer and pesticides, irrigations, aeration, and mowing required to maintain healthy, playable turfgrass (Turgeon, 1996; Witteveen and Bavier, 1999; King and Balogh, 2006). According to the Golf Course Superintendents Association of America, the average golf course uses approximately 74 kg of phosphorus (P) per hectare of managed turf per year (Pimentel et al., 1991; USGS, 2006; GCSAA, 2009). This amount is more than twice that used in the agricultural sector and contributes to the degradation of surface waters by eutrophication (USGS, 2006; GCSAA, 2009). Although there is no comprehensive data set for annual pesticide use on golf courses, a few case studies have estimated an average usage between 4 and 270 kg a.i. ha$^{-1}$ yr$^{-1}$ (Kriner, 1985; Merrigan et al., 1996; Joyce, 1998; Schueler, 2000; Haith and Duffany, 2007; Magri and Haith, 2009). In contrast, the agricultural sector averages between 1 and 3.5 kg a.i. ha$^{-1}$ yr$^{-1}$ (Pimentel et al., 1991; USGS 2006; Haith and Duffany, 2007; Magri and Haith, 2009). As with fertilizers, excess pesticides and their residuals degrade surface water quality and can adversely affect aquatic species, birds, and humans (Cohen et al., 1999; Moore et al., 2002, Rohr et al., 2006).

Golf courses are particularly vulnerable to P and pesticide loss because of the sandy, porous grass rooting media used and the presence of subsurface tile drainage (Pira, 1997; Marshall et al., 2001; Shuman, 2003; Soldat and Petrovic, 2008). The rooting media and tile lines promote rapid infiltration and removal of excess water from the course (Reddy et al., 1978; Mansell et al., 1985). Tile drainage also helps to maintain necessary water table depths for plant growth and sufficient soil void space to prevent soil compaction and rutting (King et al., 2006). The intended effect is to enhance turf playability, especially under seasonally saturated conditions and after storm events (Sims et al., 1998; Dils and Heathwaite, 1999; King et al., 2006; Algoazany et al.,

Abbreviations: CKD, cement kiln dust; CS AC, coconut shell–activated carbon; DOC, dissolved organic carbon; EC, electrical conductivity; GBFS, granulated blast furnace slag; MDL, method detection limit; TSS, total suspended solids.

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*Corresponding author (sheela.agrawal@ars.usda.gov).
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5585 Guilford Rd., Madison, WI 53711 USA
could potentially be recycled as slow-release P fertilizers once their removal capacities have been exhausted (Bansiwal et al., 2006; de-Bashan and Bashan, 2007; Bird and Drizo, 2009).

In this study, we investigated the ability of a blend of four industrial byproducts—blast furnace slag, cement kiln dust, coconut-shell activated carbon—and two natural materials—zeolite (as clinoptilolite) and silica sand—to remove dissolved P and three pesticides—chlorothalonil (2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile), propiconazole (1-[(2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl) methyl]-1H,1,2,4-triazole), and mefenoxam ([R]-2-[(2,6-dimethylphenyl) methoxyacetylamino] propionic acid methyl ester)—from a tile-drained practice golf green under storm-simulated conditions. Ultimately, we aimed to indentify inexpensive materials for use in removing P and pesticides from tile drainage without compromising overall effluent water quality.

**Materials and Methods**

**Industrial Byproducts and Minerals**

The materials used and their sources are listed below. These materials were chosen based on their hydraulic conductivities determined in previous laboratory batch tests and as reported in the literature. Also, these materials did not leach appreciable quantities of heavy metals like Hg, Cd, and As. Each material’s properties are shown in Table 1.

2. Cement kiln dust (CKD): Larfarge North America, Michigan
3. Zeolite (clinoptilolite): St. Cloud Mining Company, New Mexico
5. Silica sand (99.5%): Fairmount Minerals and Subsidiaries, Best Sand, Ohio

**Site Description and Filter Design**

Ridgewood Country Club is a private, regulation length, 18-hole golf course located in Waco, TX, that has been in operation since 1946. The course spans a total of 0.69 km² and has a USGA rating of 71.4 and a slope rating of 128 on Bermuda grass. Runoff and drainage from the course ultimately enters nearby Lake Waco, which is a well known, nutrient-polluted surface water body (Dworkin, 2003).

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**Table 1. Material properties.**

<table>
<thead>
<tr>
<th>Material†</th>
<th>Particle diameter</th>
<th>pH</th>
<th>Bulk density</th>
<th>Total surface area</th>
<th>Chemical composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mm</td>
<td></td>
<td>g cm⁻³</td>
<td>m² g⁻¹</td>
<td>SiO₂, Al₂O₃, Fe₂O₃, CaO</td>
</tr>
<tr>
<td>GBFS‡</td>
<td>2.00–2.80</td>
<td>9.5–10.2</td>
<td>1.3–1.5</td>
<td>450–550</td>
<td>33–42, 10–16, 0.5, 36–45</td>
</tr>
<tr>
<td>Zeolite</td>
<td>2.40–3.40</td>
<td>7.5–8.0</td>
<td>0.74</td>
<td>≤800</td>
<td>70, 12.1, 1.6, 3.4</td>
</tr>
<tr>
<td>Silica sand</td>
<td>0.30–0.50</td>
<td>7.0</td>
<td>1.6</td>
<td>0.04</td>
<td>99.6, 0.134, 0.083, 0.015</td>
</tr>
<tr>
<td>CS AC</td>
<td>0.6–1.70</td>
<td>9.0</td>
<td>0.48</td>
<td>1200</td>
<td>n/a, n/a, n/a, n/a</td>
</tr>
<tr>
<td>CKD</td>
<td>&lt;0.075</td>
<td>11.0–12.0</td>
<td>1.19</td>
<td>0.9</td>
<td>15.3, 4.7, 2.2, 55.3</td>
</tr>
</tbody>
</table>

† CKD, cement kiln dust; CS AC, coconut shell–activated carbon; GBFS, granulated blast furnace slag.
§ n/a, not applicable.
The course is home to a 740-m² (8000 ft²) experimental chipping green that was originally designed to test alternative materials for the gravel subsurface construction layer. Below the surface, the green is split into discrete 370 m² (4000 ft²) halves, each of which has its own separate drainage network to allow for investigation of the alternative construction materials. For this study, only the north half of the green is considered.

The main drain tile from the north green is routed into a 3.05 m × 3.05 m × 2.44 m covered sump located about 20 m south of the southern-most tip of the green. Within the sump, the North drain tile is directly plumbed into a PVC filter box measuring 0.92 m × 0.92 m × 0.46 m. Drainage water from the North green enters the filter box through a 10.16-cm-diameter inlet pipe and moves radially through three removable filter cartridges (each cartridge has a diameter of 200 mm and is 600 mm long) before exiting through a 20.32-cm-diameter outlet. The outlet is located 0.92 m directly opposite the inflow port and was fitted with a 20.32-cm compound, v-notch weir to determine flows during storm simulation. Flow into and out of the filter cartridges was distributed as evenly as possible using flow-control baffles on either end of the filter box (Fig. 1).

The filter set-up was designed by KriStar Enterprises, Inc. (Santa Rosa, CA) and was previously used by King et al. (2010) for a smaller-scale laboratory simulation. In the present study, the filter media used in each cartridge was a 14-L blend made up of 3.5 L GBFS, 3.5 L zeolite, 3.5 L CS AC, and 3.5 L of a 5% CKD/95% sand mixture. The volumes of each material used were chosen arbitrarily, with the exception of CKD, which was mixed with sand to ensure sufficient permeability; CKD in excess of the 5% used for the sand blend tended to obstruct flow. The 14-L blend was manually mixed and weighed approximately 15 kg. Filter cartridges were filled based on volume because weighing out large quantities of the filter materials in the field was not feasible.

Experimental Design
A total of two 6-h storm simulations were conducted at the Ridgewood Country Club experimental green at mid-morning on 14 and 15 Oct. 2009. A control simulation, in which no filter media was placed in the cartridges, was run on Day 1 to determine whether the PVC filter box influenced contaminant removal. On Day 2, the empty cartridges were swapped out for new ones filled with the byproduct and mineral filter blend. Differing only in the absence or presence of filter media, the Day 1 (without filter media) and Day 2 (with filter media) runs received the same fertilizer, pesticide, and irrigation treatments as described below. Water sampling was conducted using a before-and-after, repeated measures design.

Phosphorus in the form of PO₄³⁻ (16–25–12, The Andersons Turf Fertilizer; PBI/Gordon Corp., Kansas City, MO), chlorothalonil (Lesco Manicure; GB Biosciences Corp., Greensboro, NC), mefenoxam (Quali-Pro Mefenoxam 2AQ; Nation’s Ag, LLC, Burr Ridge, IL), and propiconazole (Quali-Pro Propiconazole 14.3; Nation’s Ag) were applied to the green each day, in a single application, according to the manufacturers’ specifications and allowed to equilibrate for 30 min before storm event simulation. The total loads of PO₄³⁻, chlorothalonil, mefenoxam, and propiconazole applied to the green each day were 2.3 kg, 340.19 g, 113.40 g, and 36.95 g, respectively.

After the 30-min equilibration period, the green was irrigated with approximately 3785 L of municipal water for 10 min to simulate a storm event. Three irrigation events in total, spaced 2 h apart, were performed each day. Thus, a total of approximately 11,355 L or irrigation water was used each day. Within 5 min of irrigation, the filter cartridges in the box were submerged, allowing for sampling and flow measurements to begin. An Isco 4230 Bubbler Flow Meter (Teledyne Isco, Inc., Lincoln, NE) collected flow data in 1-min intervals for the duration of the control and experimental runs. The bubbler continued to collect flow data for an additional 8 h on the completion of each run to ensure proper delineation of the control and experimental hydrographs.

Water samples were collected by two Isco 6712 portable, automated samplers (Teledyne Isco, Inc.) that were programmed to separately but simultaneously collect 1-L samples.
of drainage water from the inlet (prefilter interaction) and outlet (postfilter interaction) of the filter box at predetermined time intervals. A simultaneous sampling design was chosen based on the assumption that high incoming flows produce negligible retention time (<1 min) within these particular filter cartridges. King et al. (2010) made a similar assumption using the same filter cartridge design in a prior laboratory study.

The samples were collected into acid-washed, preirr atmospheres, 1-L mason jars with Teflon-lined lids at 5-, 10-, 15-, 20-, 25-, 30-, 45-, 60-, and 90-min intervals postirrigation. At 2 h, the green was again irrigated for 10 min. Sampling resumed 5 min after this second irrigation and at the same intervals as previously described. This entire procedure (irrigation and sampling) was repeated a third time at the 4-h mark. Sampling ended after a total run time of 6 h. A total of 27 repeated measures samples were collected for each (Day 1 and Day 2) run.

In between sampling and irrigation intervals, the mason jars were individually removed from the samplers to measure temperature, pH, and electrical conductivity (EC). Dissolved organic carbon (DOC) and total suspended solids measurements were made at the USDA ARS facility. One-liter grab samples of irrigation water were collected and measured for each storm event simulation to correct for background contributions to drainage water chemistry. At the end of each 90-min sampling interval, all jars were collected and packed in coolers with ice for overnight shipping to the USDA ARS facility (Columbus, OH).

Sample Analyses

Upon arrival, samples were unpacked and stored below 4°C. The samples were analyzed for PO$_4$$^-$, chlorothalonil, mfenoxam, and propiconazole within 28 d. Before analysis, samples were vacuum filtered through a 0.45-μm pore diameter glass fiber membrane.

Phosphate concentrations in water samples were determined colorimetrically by the ascorbic acid reduction method using a QuickChem 8000 FIA automated ion analyzer (Lachat Instruments, Milwaukee, WI) (Parsons et al., 1984; USEPA, 1995). The detection limit (MDL) for PO$_4$$^-$ was 0.003 mg L$^{-1}$.

Dissolved organic carbon concentrations were determined by the heated persulfate oxidation method on an Aurora 1030W Total Organic Carbon Analyzer (O I Analytical, College Station, TX) with in-line sample acidification and sparging (MDL = 0.04 mg L$^{-1}$) (USEPA, 1995; Eaton et al., 1998). Total suspended solids (TSS) measurements were determined by the change in mass of a preweighed, 45-μM glass fiber filter.

Chlorothalonil, mfenoxam, and propiconazole residues were determined using a Saturn 2200 gas chromatography mass spectrometer (Varian, Inc., Palo Alto, CA) (USEPA, 1995); MDL values were 0.098, 0.10, and 0.01 μg L$^{-1}$ for each pesticide, respectively. Before pesticide extraction, each filtered sample was fortified with 1 mL of methanol and a terbutylazine standard (final concentration = 500 μg L$^{-1}$). The samples were then extracted using 10-mL Bond Elut C-18 cartridges (Varian) preconditioned with methanol. After a 45-min air-drying period, each cartridge was eluted with four 0.5-mL aliquots of ethyl acetate, dried under N$_2$ gas, and reconstituted with 1 mL ethyl acetate containing acetonaphthalene (final concentration, 500 μg L$^{-1}$) as an internal standard. The extracted samples were then frozen at or below 0°C until gas chromatography–mass spectrometry analysis. During analysis, 2 μL of each sample was injected by splitless mode into a CP-Sil 8 CB low bleed column (30 m × 0.25 mm ID) (Varian) using a CP-8400 autosampler (Varian). Helium was the carrier gas at a flow rate of 1 mL min$^{-1}$. The oven temperature program ramped from 55 to 300°C at various time intervals with an injector temperature of 280°C. Extract composition was determined with the mass spectrometer and monitoring the masses for chlorothalonil (mass-to-charge ratio [m/z] = 266), mfenoxam (m/z = 206), and propiconazole (m/z = 259). Matrix spikes were prepared by adding a concentrated mixture of the analytes (chlorothalonil, mfenoxam, and propiconazole) to ultrapure water for a final concentration of 500 μg L$^{-1}$. Mean extraction recoveries and 95% confidence intervals for chlorothalonil, mfenoxam, and propiconazole control matrix spikes were 86 ± 18%, 90 ± 25%, and 91 ± 10%, respectively.

All statistical analyses were performed using SigmaPlot 10 (SysStat Software, Inc., Chicago, IL). The Wilcoxon signed rank test for paired data was used to delineate the effect of the filter media on the pH, DOC concentration, TSS, EC, and the efficiency of contaminant removal from the drainage water. The Mann-Whitney rank sum test was used to compare flow and load differences between and within days.

Results

For both runs, water temperature of the inflow drainage water (prefilter interaction) and outlet (postfilter interaction) remained constant. Similarly, pH, DOC concentration, TSS, and EC of the irrigation water did not fluctuate between days. It also appeared that the PVC material used to construct the filter box did not remove contaminants because there was no difference in prefiltter and postfilter loads for all contaminants in the Day 1 (without filter media) control run ($P > 0.05$).

The differences in pre- and postfilter TSS concentrations (mg L$^{-1}$) for both runs were not statistically significant ($P > 0.05$), suggesting that the filter treatment does not change effluent water quality with respect to TSS. In contrast, changes in pre- and postfilter interaction EC measurements (mS cm$^{-1}$) were statistically significant, suggesting that the filter media did influence EC, specifically by increasing it. However, this increase did not adversely affect overall effluent water quality (Table 2).

Table 2. Comparison between typical surface water quality parameter values and study values.†

<table>
<thead>
<tr>
<th>Water quality parameter‡</th>
<th>Typical surface water parameter values</th>
<th>Study values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.8–8.6</td>
<td>6.75 ± 0.32</td>
</tr>
<tr>
<td>DOC, mg L$^{-1}$</td>
<td>1.00–20.0</td>
<td>10.42 ± 0.77</td>
</tr>
<tr>
<td>EC, mS cm$^{-1}$</td>
<td>0.05–1.5</td>
<td>0.20 ± 0.11</td>
</tr>
<tr>
<td>TSS, mg L$^{-1}$</td>
<td>0–263§</td>
<td>2.53 ± 1.83</td>
</tr>
</tbody>
</table>

‡ DOC, dissolved organic carbon; EC, electrical conductivity; TSS, total suspended solids.
§ Values represent the range of acceptable concentrations in discharged waters between the four states in the United States (Hawaii, Utah, North Dakota, and South Dakota) that have TSS standards. The USEPA does not regulate TSS.
Statistical differences in the pH and DOC concentrations of pre- and postfilter interaction samples were not as clearly delineated. For example, significant changes in pH were observed on Day 1 (without filter media) and Day 2 (with filter media), thus making it difficult to discern the effects of the filter media on pH. However, despite these discrepancies, the differences observed for both runs did not negatively affect water quality. In other words, all pH and DOC values fell within their respective ranges for good effluent water quality. The pH across both runs averaged 6.75 ± 0.32 mg L⁻¹ (SD), whereas DOC averaged 10.42 ± 0.77 mg L⁻¹ (Table 2).

Drainage inflow rates differed significantly between Day 1 (without filter media) and Day 2 (with filter media), with the higher median flow rate occurring on Day 1 (0.138 L s⁻¹), than on Day 2 (0.108 L s⁻¹) (P < 0.001). The differences in flow over time between the days can be seen in Fig. 2. In sequential order, peak flows for Day 1 were 0.643 L s⁻¹ (at t = 3600 s), 0.643 L s⁻¹ (t = 9600 s), and 0.554 L s⁻¹ (t = 18600 s), respectively. Peak flows for Day 2 were 0.234 L s⁻¹ (t = 2700 s), 0.583 L s⁻¹ (t = 9300 s), and 0.628 L s⁻¹ (t = 16 500 s), respectively.

Prefilter contaminant loads also differed between the 2 d. For example, the magnitude of the cumulative prefilter PO₄³⁻ load on Day 1 was 3580 mg, whereas that of Day 2 was 3086 mg. Conversely, the magnitudes of mefenoxam, propiconazole, and chlorothalonil loads were greater on Day 2 vs. Day 1. Day 1 prefilter cumulative loads of mefenoxam, propiconazole, and chlorothalonil were 148, 3, and 38 mg, respectively, whereas those on Day 2 were 416, 10, and 98 mg, respectively.

Influent (prefilter interaction) contaminant loading rates varied with drainage flow rate. Phosphate exhibited the clearest trend, with its loading rate increasing as a function of flow rate (Fig. 3). This trend was less clear for propiconazole, chlorothalonil, and mefenoxam (Fig. 3).

Despite the variability in flow rates and contaminant prefilter loading rates, a real decrease in the chlorothalonil load was observed for Day 2 (with filter media) when compared with Day 1 (without filter media) (P < 0.001). The median decrease in chlorothalonil for the Day 2 load was 69% (average and 95% confidence interval, 57 ± 13%), whereas that of the control was 0%. The highest reduction of chlorothalonil was 96% and occurred at time = 45 min (2700 s), flow = 0.234 L s⁻¹, and a prefilter chlorothalonil load = 4.06 mg. Percent chlorothalonil removed as a function of time and flow rate is seen in Fig. 4. In general, chlorothalonil removal was very high (>80%) near peak flows.

Significant quantities of chlorothalonil were also removed at even higher flow rates than 0.234 L s⁻¹. For example, 94 and 87% of chlorothalonil were removed at flow rates of 0.583 L s⁻¹ and 0.540 L s⁻¹, respectively. Furthermore, contaminant loads at these flow rates were significantly greater than at 0.234 L s⁻¹ (t = 45 min), and thus larger absolute loads of chlorothalonil were removed.

In contrast, reductions in PO₄³⁻, mefenoxam, and propiconazole between the Day 1 and Day 2 runs were not statistically different (P > 0.05). Instead, it appears that the filter media blend added in excess of 146% of the incoming PO₄³⁻ load to the effluent. The addition of PO₄³⁻ to the effluent by the filter media will herein be referred to as “offloading.” The cumulative PO₄³⁻ load before filter interaction was 3086.10 mg, whereas that of the effluent was 7605.29 mg. The total amount of PO₄³⁻ offloaded per kilogram of filter media for Day 2 was 300 mg kg⁻¹.

However, samples with flow rates below 0.037 L s⁻¹ (the first five samples collected postirrigation) exhibited statistically significant reductions in PO₄³⁻ between prefiltered and filtered water (and compared with Day 1 samples) (P < 0.001). The mean percent reduction in PO₄³⁻ (with a 95% confidence interval) for this low flow interval was 22 ± 4.5%. This amounted to only a 0.19% reduction in the total incoming P load over the course of the run and was far outweighed by the 146% PO₄³⁻ increase in the filtered water. For flow rates greater than 0.037 L s⁻¹, the PO₄³⁻ offloading rate was positively correlated with flow rate (Fig. 5).

Discussion

Previous research has identified zeolite, CS AC, GBFS, CKD, and to some extent silica sand, as suitable PO₄³⁻ sorbents (Johansson and Gustafsson, 2000; Oguz, 2004, 2005). However, in this study, despite favorable drainage pH to support PO₄³⁻ removal, it appears that high inflow rates, especially those greater than 0.037 L s⁻¹, limited contact time with these materials and thus PO₄³⁻ removal. McDowell et al. (2008) observed a similar high flow/short contact time trend in the end-of-fluvium filter sock investigation previously mentioned. The authors also attribute the observed low P removal to the small quantity, and ultimately small surface area, of filter
material used. In contrast, Korkusuz et al. (2005) averaged 44% PO$_4^{3-}$ removal from wastewater, flowing at 2.1 L s$^{-1}$, by using over 11 Mg of slag. On an even larger scale, Shilton et al. (2006) used nearly 19 Gg slag over a 5-yr period to capture 77% P from wastewaters averaging flows of 1389 L s$^{-1}$ (retention time on the filters was approximately 3 d). Although these last two studies used slag-based filters, the results nonetheless support the idea that a very large quantity of filter media is necessary to accommodate high incoming flows. Thus, it may be that the current study’s filter system should be completely redesigned or modified to incorporate significantly larger quantities of the investigated filter materials.

The 0.19% PO$_4^{3-}$ removal was dwarfed by the 146% increase in the effluent PO$_4^{3-}$ load beyond the 0.037 L s$^{-1}$ flow threshold. The quantity of PO$_4^{3-}$ offloaded per kilogram of filter media was significantly greater than that observed in bench-scale, leachate batch experiments conducted before this study for the same blend (refer to USEPA [2008] for batch experiment method). The materials in the current study offloaded approximately 300 mg PO$_4^{3-}$ per kilogram of filter media, compared with 5 mg kg$^{-1}$ in the batch experiments. In the batch experiments, a fixed volume of water was in contact with the filter blend in slowly rotating Teflon test tubes such that flow out of the system did not occur. Because this same water was always in contact with the filter media, flow rate was considered to be negligible compared with the current study. Thus it appears that flow rate affected not only the efficacy of contaminant removal but also the degree of PO$_4^{3-}$ offloading.

It is not known which material or materials in the filter blend are offloading PO$_4^{3-}$. Because this blend is unique to this study, it has not been characterized by others. However, PO$_4^{3-}$ offloading has been observed for some filter medium constituents, namely slag. Shilton et al. (2006), for example, documented an increase in effluent PO$_4^{3-}$ after 5 yr of slag-based, continuous filtration because of filter saturation. Whether the authors observed a large initial flush of PO$_4^{3-}$ is unknown. With respect to the current study, further investigation is needed to determine which filter media constituent or constituents

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**Fig. 3.** Day 1 (control run, without filter media) and Day 2 (experimental run, with filter media) PO$_4^{3-}$, chlorothalonil, mefenoxam, and propiconazole loading rates (mg s$^{-1}$) as a function of flow rate (L s$^{-1}$).
are offloading $\text{PO}_4^{3-}$, whether it continues to offload $\text{PO}_4^{3-}$ over time before saturation, and how much $\text{PO}_4^{3-}$ can be accommodated before filter saturation.

Chlorothalonil removal was extremely high for high incoming flows, which is in contrast to the observations reported by King et al. (2010). In their investigation, the highest percent removals of chlorothalonil were seen during the rising and receding limbs of the generated hydrographs. The reason for chlorothalonil's behavior in the present study is unclear, but it may be due to the different types of materials used (with the exception of zeolite) in the present study versus those used by King et al. (2010).

The variability in pesticide removal in the present study is a reflection of not only the high incoming flow rates and the amount of material used but also of each pesticide's physical and chemical properties (Lyman et al., 1990; Mackay et al., 2006). The water solubilities ($C_s$) and partition coefficients ($\log K_{oc}$) of mefenoxam ($C_s = 100 \text{ mg L}^{-1}$; $\log K_{oc} = 1.46$–2.46) and propiconazole ($C_s = 26 \text{ g L}^{-1}$; $\log K_{oc} = 2.59$–3.06) differ significantly from those of chlorothalonil ($C_s = 0.6 \text{ mg L}^{-1}$; $\log K_{oc} = 3.20$–4.15) and may thus account for their comparatively insignificant removal (Gardner and Branham, 2001; Marrs and Ballantyne, 2004). That is, propiconazole and mefenoxam are significantly more soluble than chlorothalonil, whereas chlorothalonil exhibits a greater tendency to sorb to soils. Again, optimizing the filter blend or changing the design could improve propiconazole and mefenoxam removal.

Although the GBFS, CS AC, CKD, sand, and zeolite filter blend removed chlorothalonil but not $\text{PO}_4^{3-}$, mefenoxam, or propiconazole, it should still be pursued for large-scale implementation, especially because of the ease of acquisition of its constituents and good performance in prior batch experiments and other larger-scale investigations. Moreover, with the exception of $\text{PO}_4^{3-}$ offloading, the blend did not adversely affect effluent water quality. Further investigation is needed to determine the optimum blend of byproducts and minerals needed to remove significant quantities of $\text{PO}_4^{3-}$, chlorothalonil, and mefenoxam as well as other contaminants of interest. In general, larger quantities of the filter material or a new filter design are needed to accommodate the green's high drainage flows to allow for sufficient contact time for contaminant removal.

References


