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FGD Gypsum Filters Remove Soluble Phosphorus from Agricultural Drainage Waters.

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INTRODUCTION

The Delmarva Peninsula houses a robust poultry industry that has been scrutinized for its contributions of nutrients to the Bay. Decades of chicken litter applications have led to phosphorus (P) levels up to ten times the agronomic optimum in soils on the Delmarva Peninsula. This legacy P is a major source of P entering drainage ditches that empty into streams and rivers that eventually flow to the Chesapeake Bay. University of Maryland Eastern Shore (UMES) and USDA-Agricultural Research Service (ARS) researchers have documented substantial P concentrations in agricultural drainage waters derived from these high P soils (350 to 550 mg kg^{-1} Mehlich-3 P). Even when fields receive no P additions, losses due to soluble P in waters draining from these high P soils result in P concentrations in ditches of 2 to 4 mg L^{-1}. Loads can vary widely in response to precipitation patterns, but annual P losses of 25 kg ha^{-1} are common.

Existing conservation practices, such as minimum tillage and edge-of-field grass filter strips, are designed to reduce sediment-bound, particulate P in runoff and offer no control over soluble P losses. Eliminating future litter applications will do little to reduce P losses in the near term, as it will require decades of cropping without P additions to deplete existing soil P reserves. In this study, our strategy for controlling soluble P losses is to intercept the flow path using a relatively low value coal combustion product to sorb soluble P, thereby removing it from agricultural drainage waters leaving the farm. Specific objectives are to design, build, and monitor the effectiveness of an in-ditch filter to remove soluble P by precipitating it as calcium phosphate, thereby reducing P losses from upstream agricultural fields.

STUDY SITE

The on-going study is being conducted on the University of Maryland Eastern Shore's Research and Teaching Farm, which was formerly a commercial poultry farm, located near the city of Princess Anne in Somerset County, Maryland. The UMES Research and Teaching Farm lies in the heart of the poultry producing area and has some of the highest soil P values on the Eastern Shore in close proximity to the Chesapeake Bay.

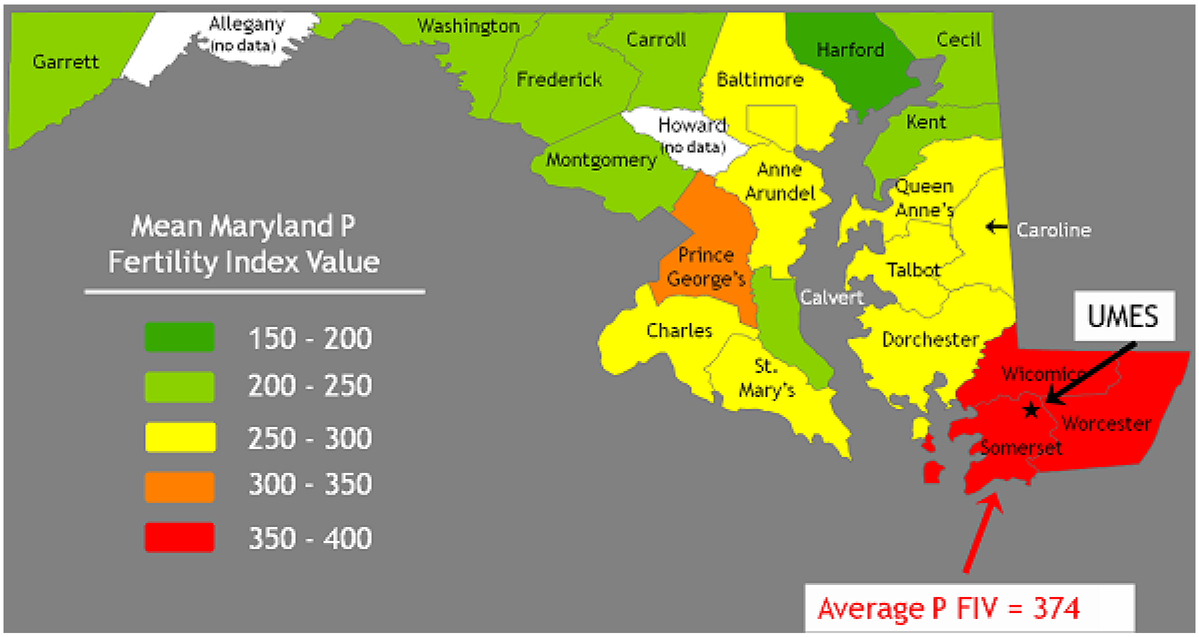

Figure 1. Location of study area and mean Maryland P fertility index values (FIV) for soils over 100 FIV (equivalent to Mehlich-3 P values) by county.

DITCH FILTER CONSTRUCTION

In April, 2007, one of the larger collection ditches, bounded on both sides by poultry houses and soils with Mehlich-3 P values averaging 450 mg kg^{-1}, was selected as the construction site for the ditch filter (Fig. 2). The ditch drains approximately 17 hectares. In order to establish a hydrologic head above the filtration bed, ditch flow is impeded by a compound straight-walled, V-notch weir, which was used to measure bypass flow during large flow events when drainage waters overtop the weir. Flue gas desulfurization (FGD) gypsum was selected for use as the sorbing agent. The solubility of the gypsum ($CaSO_4{\cdot}2H_2O$) supports a concentration of soluble calcium that reacts with soluble P to precipitate as calcium phosphate ($CaPO_4$), which is less soluble than gypsum. Five tons of sand and 120 tons of FGD gypsum were used in the construction of the filter bed. After the weir was installed, gabions were placed behind it to prevent wash out. A manifold, placed in front of the weir, is connected to a drain pipe, which routes the filtered effluent underground around the weir and through a partially buried metal box that provides access to sampling equipment. The box houses a flume that measures the rate of flow emptying from the drain pipe, and it provides access for a sampling tube connected to an automated sampler, which draws aliquots of filtered effluent for analysis. An automated sampler placed 50 m upstream collects unfiltered ditch flow. The samplers are triggered to begin sampling simultaneously when the flume detects a flow event. The filter bed consists of six 33 m long, 10 cm diameter tile lines that are encased in drain sock, attached to the manifold, and sandwiched within a layer of sand with FGD gypsum above (25 cm thick) and below (10 cm thick). A coconut fiber erosion control mat stabilizes the surface of the bed until vegetation is established by natural succession.

Figure 2. Clockwise from left: Location of the gypsum filter; 120 tons of FGD gypsum was used in construction; a weir impedes ditch flow and measures overflow (white arrows show direction of flow); six 10 cm tile lines (30 m long) attach to the manifold in front of the weir; tile lines embedded in sand are sandwiched in FGD gypsum above and below; filtered effluent is routed underground around the weir and through flow and concentration monitoring instruments before release downstream.

MATERIALS AND METHODS

The FGD gypsum used in this study was purchased from U.S. Gypsum; the source is a coal fired power plant in central Pennsylvania. Samples of fresh FGD gypsum that was used to construct the filter in April, 2007 and samples taken from the filter bed in January, 2011were digested following EPA standard method 3050b (Kimbrough and Wakakuwa, 1989) and analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES). Automated samplers were used to take water samples from the ditch upstream of the filter and from the collection pipe that routes the filtered effluent around the weir and discharges it to the ditch downstream of the filter. When the flow gauge detects a rise in water level it triggers both samplers to begin drawing samples at timed intervals during and after the event. Water samples are filtered (0.45 μ) and pH is measured at the UMES Nutrient Analysis Laboratory. Samples were shipped to the USDA-ARS Water Quality Laboratory at University Park, PA for ICP-OES analysis for the following elements and detection limits (mg L^{-1}): Al (0.01), Cd (0.01), Ca (0.1), Cu (0.01), Fe (0.01), Pb (0.01), Mg (0.01), Mn (0.01), Mo (0.01), Ni (0.01), P (0.1), K (0.1), Na (0.1), S (0.1), and Zn (0.01). Using the ICP-OES equipped with a hydride generator, detection limits for determinations of Mercury (Hg) and Arsenic (As) are 1 μg L^{-1}, suitably below drinking water standards of 2 and 10 μg L^{-1} respectively.

RESULTS AND DISCUSSION

The success of the gypsum filter as a strategy for removing soluble P from agricultural ditch drainage waters is discussed in terms of "chemical efficiency," "physical efficiency," and "environmental impact." Chemical efficiency refers to the amount of P removed from water that passes through the filter. Physical efficiency depends on the hydraulic conductivity of the gypsum bed which determines the ability of the filter to process large volumes of water during high flow events. Environmental impact is assessed in terms of the fate of Mercury (Hg) and Arsenic (As), which are the primary elements of environmental concern that are present in the FGD gypsum.

CHEMICAL EFFICIENCY

From April, 2007 to April 2010, flow and water chemistry data were collected for 34 flow events. Six flow events, one that is representative of a large (L) flow event and one that is representative of a small (S) flow event from each year of operation, are selected for discussion. Gypsum is a neutral salt and should not strongly affect pH. The pH of ditch flow in our study typically ranges from 6.0 to 6.5; pH of the effluent that passed through the gypsum filter has slightly higher pH, typically ranging from 6.5 to 7.0.

Ranges and mean values for P concentrations in unfiltered ditch flow (sampled upstream of the filter) and filtered flow (sampled from the effluent pipe) are shown in Table 1. Percent P reduction appears to vary in response to antecedent moisture conditions in the gypsum bed. Under initially dry conditions and small events of relatively short duration, percent P reduction is lower as time is required for the gypsum to become wet and dissolve sufficiently to support a high concentration of soluble calcium to react with the soluble P. It was also noted that animal burrows and root channels can provide conduits for flow that bypasses the filter bed and routes water directly to the buried drain tiles. In spite of this variability, the mean P reduction over 34 events was approximately 75 %.

Table 1. Soluble P reductions in storm water that passed through the gypsum filter.

Date	Unfiltered P (mg L^{-1}) Range	Unfiltered P (mg L^{-1}) Mean (n)	Filtered P (mg L^{-1}) Range	Filtered P (mg L^{-1}) Mean (n)	P Reduction
04/13/2007 (S)	0.03 - 0.07	0.05 (24)	0.01 - 0.08	0.04 (24)	24%
04/18/2007 (L)	0.07 - 1.75	1.11 (24)	0.01 - 0.04	0.23 (24)	79%
06/08/2008 (L)	1.61 - 2.12	1.84 (9)	0.04 - 0.61	0.33 (20)	82%
07/04/2008 (S)	1.38 - 2.87	1.87 (24)	0.01 - 0.53	0.16 (24)	89%
04/09/2009 (S)	0.36 - 1.50	0.86 (24)	0.42 - 1.04	0.74 (24)	22%
11/09/2009 (L)	0.70 - 1.23	1.05 (13)	0.03 - 0.08	0.04 (23)	96%

PHYSICAL EFFICIENCY

Ditch flow from small storm events and base flow after storm events are easily impounded in front of the weir and filtered through the gypsum bed. To avoid flooding, the gypsum ditch filter was designed to allow excess flow to spill over the weir and bypass the filter. As measured by the flume on the drain pipe, the maximum filtration rate during the large storm on April 18, 2007 was 4 L sec^{-1}, whereas the maximum ditch flow rate was 215 L sec^{-1}. Consequently, 93 % of the ditch flow during that event bypassed the filter (Table 2), which proved to be typical for large storm events.

Table 2. Precipitation, total, filtered and unfiltered (bypass) flow volumes for six storms.

Date	Rainfall mm	Duration hrs	Total flow L	Filtered flow L	Unfiltered flow L (%)
04/13/2007 (S)	16	6.7	16306	16306	0 (0%)
04/18/2007 (L)	66	3.5	7878666	570588	7308078 (93%)
06/08/2008 (L)	85	38	2501454	491181	2010273 (80%)
07/04/2008 (S)	34	4.1	265146	227509	37637 (14%)
04/09/2009 (S)	55	16	397852	138835	259017 (65%)
11/09/2009 (L)	119	42	12509125	564093	11945032 (95%)

The hydraulic conductivity of the gypsum decreased over time. The maximum filtration rate during a large storm on November 9, 2009 was only 1.1 L sec^{-1}. In September, 2010, we cleaned the vegetation from the filter bed and used a roto-tiller to mix the surface in an attempt to alleviate surface sealing. Following tillage, the maximum filtration rate increased to 2.7 L sec^{-1}, but it is clear that density of the gypsum bed increases and hydraulic conductivity decreases over time.

ENVIRONMENTAL IMPACT

Aqua regia digests of the FGD gypsum used to construct the filter in April, 2007 showed P present at 44.6 mg kg^{-1}, mercury (Hg) at 0.05 mg kg^{-1} and arsenic (As) at 2.5 mg kg^{-1}.

Mercury can volatilize following a photoreduction reaction that occurs upon exposure to light (Nriagu, 1994). Following installation, the gypsum filter bed was covered with an erosion mat, and over time, vegetation established on the surface of the filter. Therefore, Hg losses due to volatilization are expected to be minimal, although we did not attempt to measure volatilization losses. We did not detect mercury (Hg) in any of the water samples, filtered or unfiltered, at detection limit of 1 µg L^{-1}, indicating that Hg does not leach from the gypsum at concentrations that might cause concern.

The data for arsenic (As) are summarized in Table 3. The large storm events showed that filtration actually results in lower concentrations of As; reductions ranged from 37 to 97 percent. For small storms, As was not detected in 2007; we observed a 37% reduction in As concentration in 2008; and in 2009 we observed a 19% increase in As concentration after filtration. These data illustrate the variability in results that we can expect due to differences in management and climatic conditions prior to and during a flow event. However, the data suggest that soluble arsenate is being precipitated as calcium arsenate as it passes through the high calcium environment of the gypsum filter. Whereas the solubilities of gypsum, arsenic in calcium arsenate, and P in calcium phosphate are 2.1 g/L, 0.1 g/L and 0.005 g/L respectively, we can expect As and P to remain insoluble as long as gypsum is present.

Table 3. Soluble arsenic (As) reductions in storm water that passed through the filter.

	Unfiltered As (µg L^{-1})		Filtered As (µg L^{-1})		As
Date	Range	Mean (n)	Range	Mean (n)	Reduction
04/13/2007 (S)	n. d.	0 (24)	n. d.	0 (24)	---
04/18/2007 (L)	2 - 6	4.0 (24)	0 - 4	1.6 (24)	60%
06/08/2008 (L)	4 - 4	4.0 (9)	0 - 5	2.6 (20)	37%
07/04/2008 (S)	3 - 7	3.5 (24)	0 - 5	2.6 (24)	25%
04/09/2009 (S)	1 - 3	2.2 (24)	2 - 3	2.6 (24)	(19%)
11/09/2009 (L)	2 - 3	2.5 (13)	n. d.	0.0 (23)	97%

Aqua regia digests of core samples taken from the gypsum bed in December, 2010 showed P present in interior of the gypsum bed at 99.2 mg kg^{-1}, mercury (Hg) at 0.10 mg kg^{-1} and arsenic (As) at 2.2 mg kg^{-1}. The two-fold increase in P content supports the conclusion based on the water chemistry data that the filter is chemically effective at precipitating soluble P and retaining P within the filter bed in stable form as calcium phosphate. The reason for the two-fold increase in Hg content in the gypsum bed is unknown as Hg concentrations in the water that entered the filter were below detection limits, and a chemical reaction resulting in the precipitation of Hg is not apparent. Actual amounts are small, thus this observation may not be significant. However, results indicate that the gypsum filter is not delivering Hg to the environment. In spite of water chemistry data that suggest that As is precipitated as calcium arsenate in the gypsum bed, the slightly lower level of As in the gypsum that was measured after over three years of filtration suggests that the gypsum filter is not very effective at reducing soluble As in ditch drainage waters. This is likely a result of competition between P and As in sorbtion and preciptiation reactions (Peryea and Kammereck, 1997), coupled with the much higher concentrations of phosphorus found in the ditch influent as compared to arsenate concentrations.

The gypsum filter also acts as a sediment trap for particulate-bound P. Aqua regia digests of samples taken from the surface (0 to 2 cm) of the gypsum bed in December, 2010 showed P present at 391.3 mg kg^{-1}, Hg at 0.9 mg kg^{-1} and As at 3.4 mg kg^{-1}. These values were excluded from the values previously reported for elemental content in the interior of the gypsum bed. When these accumulations are taken into consideration, the gypsum filter is a net sink for P, Hg, and As.

SUMMARY AND CONCLUSIONS

Three years of data provide evidence that the FGD gypsum filter is chemically effective at reducing soluble P, and there is no mercury or arsenic loss that would have a negative environmental impact. However, the physical efficiency of the gypsum filter is disappointingly low, and large P loads that move during large storm events mostly bypass the filter and flow to the receiving water body.

Subsequent research on the fate and transport of P in soils at this site showed that 90 percent of the P that reaches the drainage ditch moves laterally in groundwater when water tables are high; only 10 percent moves overland in runoff (Vadas, et al., 2007). Based on this knowledge, we propose trenching adjacent to drainage ditches and filling the trenches with FGD gypsum to intercept and treat P laden groundwater before it enters the ditch. This alternative design, referred to as the “gypsum curtain,” is currently being tested at the UMES Agricultural Experiment Station.

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