Effects of Flue Gas Desulfurization Products as Soil Amendments to Improve Water Quality

Liming Chen[1], Tara Van Toai[2], and Warren A. Dick[1*]

[1]School of Environment and Natural Resources, The Ohio State University, Wooster, OH 44691; [2]USDA-ARS, Columbus, OH 20817
*Corresponding author and presenter

KEYWORDS: arsenic, mercury, soluble phosphorus, runoff, eutrophication

ABSTRACT

Abandoned surface coal-mined lands and eutrophication of lakes are environmental concerns worldwide due to their negative impact on water quality. We investigated the use of flue gas desulfurization (FGD) products to improve water quality. In a field study, dry FGD product (i.e. atmospheric fluidized bed combustion burner product) was applied to acidic abandoned surface coal mine soil (pH 3.1) at 280 Mg ha^{-1} alone or with 112 Mg ha^{-1} yard waste compost. Conventional soil treatment (20 cm cover) served as the control. A grass-legume sward was planted, and pH and elements in runoff and tile flow water were determined as long as 17 years after treatments. The pH was increased by all treatments and was still more than 7.5 in surface runoff and 5.9 in tile flow in the 17th year after treatments. Compared with the conventional soil treatment, Ca, S and B concentrations in water were generally increased by the treatments with FGD, but concentrations of the heavy metals were generally not increased. These results suggest FGD product can effectively reclaim acidic surface coal mined lands and provide effective long-term remediation. In a greenhouse study, FGD gypsum was applied at 3.4 Mg ha^{-1} to two soils and soybeans were planted. The soils were waterlogged when soybeans were at the V2 stage of growth. FGD gypsum reduced soluble P concentration and algae growth in ponded water above the agricultural soil surfaces. It is known that gypsum can increase crop yields and our results now indicate that when used appropriately, they can also improve water quality.

INTRODUCTION

Coal mining and coal preparation practices in the years prior to the enactment of reclamation laws frequently resulted in dumping of coal cleaning refuse into large piles. Many surface mine sites were simply abandoned without adequate reclamation of iron sulfide-containing materials, the source of much of the acid mine drainage. Thus, some refuse or abandoned mine sites produce copious amounts of acid that eventually drain into many streams and rivers. Soils are also affected by the acid drainage becoming unsuitable for production of crops or use as pasture lands or woodlands. Reclamation of abandoned and active coal mine lands is a worldwide environmental concern because it impacts surface water quality, groundwater quality, revegetation and aesthetics[1].

Use of topsoil and limestone to restore coal mined land is a well-established technology, and current reclamation laws require that lands from active coal mine operations must be covered using topsoil to assist re-vegetation. However, topsoil was generally not conserved when these sites were surface mined for coal prior to the reclamation laws. Thus, soil from adjacent land is used for reclamation of abandoned surface coal mined lands so that another disturbed area is created. If sufficient borrow soil is not available adjacent to the mine site, the cost of reclaiming abandoned coal mined lands can be prohibitive unless alternative materials are identified. For example, when S-containing coal is burned in the United States, the SO_2 produced must be removed from flue gases to meet regulated emission levels. Some flue gas desulfurization (FGD) processes generate dry by-products containing reaction products of Ca-sulfates and/or Ca-sulfites together with substantial quantities of alkaline excess sorbent in the form of calcite ($CaCO_3$), dolomite [$CaMg(CO_3)_2$], lime (CaO), and/or portlandite [$Ca(OH)_2$][2]. Several studies have shown that this property enables FGD by-products to be used as alkaline amendments for acid agricultural and mine land soils[3,4,5,6].

Flue gas desulfurization gypsum is created in limestone-forced oxidation scrubbers that remove sulfur dioxide from the flue gas stream after coal combustion. Gypsum is one of the earliest forms of fertilizer used in the United States, having been applied to agricultural soils for over 250 years. It is widely accepted as a source of the essential plant nutrients, calcium (Ca) and sulfur (S), needed for good crop growth. In addition, gypsum has been used as an amendment to improve physical and chemical soil properties, as a reactant to reduce nutrient and sediment transport to water bodies, to remediate some problematic soils (e.g. sodic soils), and to overcome problems associated with acidic subsoil by binding soluble aluminum. It has also been shown to play a significant role in controlling phosphorus (P) in runoff[7].

Runoff from agricultural fields is a major source of nutrient loading in many impaired waterways in the United States. Excess nutrients are recognized as a significant problem that leads to algal blooms and eutrophication in lakes and rivers. Development of a suite of effective and economical practices to prevent loss of nutrients in runoff is the key to reducing agricultural non-point source pollution and improving water quality. Use of FGD gypsum for controlling dissolved reactive P in runoff from agricultural fields represents a win-win-win scenario. Reducing soluble P will result in less non-point source pollution and improved water quality.

The objectives of this study were to determine the effects of a dry FGD product on water quality from an acidic mine spoil and to assess its potential capacities to achieve long-term reclamation success and to determine the effects of FGD gypsum on ponding water quality.

Materials and Methods

Field experiment

The study site was located in Franklin Township, Tuscarawas County, OH (40° 33' 19" north latitude and 81° 31' 13" west longitude). Detailed information about this study site was previously provided by Chen et al.[8], and is presented here in brief. Before reclamation, the abandoned mine site consisted of approximately 10 ha of exposed, highly erodible underclay bordered on two sides by 18 ha of spoil and 2 ha of coal refuse. The spoil and refuse were mapped and classified as being a member of the Bethesda soil series (loamy-skeletal, mixed, acid, mesic Typic Udorthent). Acid drainage from the area was a significant problem with surface water pHs ranging from 2.4 to 3.9. Oxidation of pyrite (FeS_2) associated with the Middle and Upper Kittanning coal beds and underclays was a major cause of the acidity. Natural re-colonization of the site by plants was severely limited. In the autumn of 1994, six 0.4-ha plots were constructed. First, exposed underclay was graded to a 4% slope using earthmoving equipment and then compacted to create an aquitard. Thickness of the aquitard ranged from 3 m to greater than 10 m. A 1.5 m wide by 30 cm high berm was constructed from the underclay to hydrologically separate each plot. Next, 1.2 m of mine spoil from the adjacent areas was placed over the underclay and also graded to a 4% slope.

Three treatments were applied to the six plots in duplicate and included: (1) agricultural limestone incorporated at 112 Mg ha^{-1} into the graded spoil and then covered with 20 cm of borrowed soil treated with an additional 45 Mg ha^{-1} agricultural limestone; (2) FGD product incorporated at 280 Mg ha^{-1} into the graded spoil with a chisel plow to a depth of 20 cm; **(**3) FGD product at 280 Mg ha^{-1} blended with yard-waste compost at 112 Mg ha^{-1} and incorporated into the graded spoil with a chisel plow to 20 cm depth. The three treatments will hereafter be referred to as SOIL, FGD, and FGD/C treatments, respectively. The FGD product came from an atmospheric fluidized bed combustion burner at a General Motors plant in Pontiac, MI. The yard-waste (grass clippings and woody mulch) compost was obtained from Earth-N-Wood, Inc. of North Canton, OH. The borrowed soil was obtained from a designated area north of the study site. Selected properties of these amendment materials were described in Chen et al.[8]. The application rates were based on the lime test index (SMP buffer pH x 10) of the spoil. In order to adjust the pH to 7, the Ohio Agronomy Guide[9] recommended adding 112 Mg ha^{-1} of limestone with 100% calcium carbonate equivalent (CCE). Since the FGD product had a CCE of approximately 40%, its application rate had to be adjusted to 280 Mg ha^{-1} to provide neutralization potential equivalent to that of pure limestone. The plots were seeded in November 1994 using a seed mixture consisting of orchard grass (*Dactylis glomerata*), timothy (*Phleum pratense*), annual ryegrass (*Lolium multiflorum*), ladino clover *(Trifolium repens*e Ladino), birdsfoot trefoil (*Lotus corniculatus*) and winter wheat (*Agropyron* sp.).

In 1996, runoff and tile flow were collected periodically from April to October during the plant growing season. In 2011, runoff and tile flow were collected only on April 25. Runoff samples were collected from the six small watersheds created on the experimental site after each precipitation event that produced runoff. Tile flow was obtained from the tile outlet installed at the downslope end of each watershed (Fig. 1). Water samples were analyzed for pH, electrical conductivity (EC) and concentrations of elements after filtering through a 0.45 µm membrane filter. Concentrations of elements in the water were determined by inductivity coupled plasma atomic emission spectrometry (ICP-AES).

Greenhouse experiment

A greenhouse experiment to study the effects of gypsum and flooding on water quality was conducted at the Ohio Agricultural Research and Development Center of The Ohio State University located in Wooster, Ohio. Treatments included two types of soil (sandy and clay soils), two rates of gypsum (0 and 3360 kg ha^{-1}), two soybean cultivars (Wooster and Wyandot), and two rates of flooding (without flooding and 11-day flooding). These 16 treatments were arranged in a randomized block design with three replicates. Soils were put in 11 L plastic pots and placed in a greenhouse. Fertilizer (6-26-26) of 1.33 g and FGD gypsum of 13.3 g was incorporated into the 2.5 cm soil layer. Elements in soils and FGD gypsum are presented in Table 1. Five seeds were planted in each pot at 2.5-cm depth. The greenhouse was maintained at 22-25^{o} C for day time and at 18-21^{o} C for night time. Fluorescent and incandescent light was provided for 14 h. The pots were watered with tap water every day.

One month after planting, three soybean plants were kept in each pot. In each treatment, the tap water was applied slowly to three pots until ponding, and other three pots were watered as needed. After that day, water was added frequently to the ponded pots because of water infiltration and evaporation, so that there was always some ponding in the pots. Five days after ponding, pictures for algae growth in ponding water were taken. Seven days after ponding, ponding water samples were collected, and concentrations of P in ponding water were determined by ICP-AES.

Statistical analysis

The results in this study were analyzed statistically using a model that included treatment as independent variables. Data were subjected to analysis of variance (ANOVA) using the PROC GLM statement of the SAS statistics program[10]. When the analysis generated a significant F value ($P \leq 0.05$) for treatments, the means were compared by the least significant difference (LSD) test using the appropriate error term to calculate the LSD value.

RESULTS AND DISCUSSION

Field experiment - Chemical properties of surface runoff water

All treatments were effective in raising pH in surface runoff in 1996 and 2011 (Table 2). It should be noted that the experimental site spoil pH prior to reclamation averaged 3.1. In fact, surface runoff pH was higher for the FGD treatment than for SOIL treatment in 1996. Addition of compost buffered the increase of water pH. In 1996 and 2011, surface runoff EC was much higher for the FGD and FGD/C treatments compared to the SOIL treatment. This outcome was undoubtedly due to the substantial amount of moderately soluble anhydrite ($CaSO_4$) and small quantities of more soluble salts that comprised the FGD product[2]. There were no significant differences in EC between the treatments of FGD and FGD/C in 1996. However, compared with the FGD treatment, the EC was lower for the FGD/C treatment. Increased pH buffering and decreased EC were expected for the FGD/C treatment because addition of an organic amendment should increase the cation exchange capacity of the material.

Calcium, S, K and Mg are essential macronutrients for higher plants. Concentrations of Ca and S, the major elements in the FGD product, in the runoff were significantly increased for the FGD or FGD/C treatment as compared to the SOIL treatment in both 1996 and 2011 (Table 2). Concentrations of Mg and K in the runoff were also significantly greater when mine soil was reclaimed with FGD and FGD/C compared with mine soil treated with SOIL in1996 and but there were no differences in 2011. Concentrations of Ca, S, Mg, and K generally decreased for the FGD/C treatment as compared to FGD treatment.

Boron, Fe and Mn are essential nutrients for higher plants, but Al is a nonessential element for most higher plants. Compared with the runoff from SOIL treatment, the surface runoff from mine soil treated with FGD or FGD/C had greater concentrations of B in 1996 and 2011 and Al in 1996 (Table 2). However, there were no significant differences for the concentrations of Fe between treatments in 1996 and 2011. Concentrations of Mn were increased for the FGD/C treatment as compared to the FGD and SOIL treatments in 1996. In both 1996 and 2011, there were no significant differences in the concentrations of RCRA-regulated elements such as As, Cd, Pb, Hg and Se among treatments (Table 3). However, compared with the SOIL treatment, concentrations of Ba were increased for the FGD and FGD/C treatments in 2011 and concentration of Cr was increased for the FGD treatment in 1996.

Field experiment - Chemical properties of tile flow water

The pH in tile flow in 1996 was increased for the FGD treatment compared to the SOIL and FGD/C treatments (Table 4). There was no different in pH among treatments in 2011. In fact, the pH in tile flow was higher at an average of 7.58 in 1996 than at an average of 5.98 in 2011. In 1996 and 2011, the EC in tile flow was much higher for the FGD treatment compared to the SOIL treatment. There were no significant differences in EC between the treatments of FGD and FGD/C in 1996 and 2011.

Concentrations of Ca and S in tile flow for the FGD and FGD/C treatments were significantly higher than for the SOIL treatment in 1996, but there were no significant differences in S concentrations among treatments in 2011 (Table 4). Concentrations of K and Mg in tile flow were significantly higher for the FGD and FGD/C treatments than the SOIL treatment in 1996 but not in 2011. Due to K binding by the compost, K concentration in the tile flow was lower for the FGD/C treatment than the FGD treatment in 1996.

Concentration of Al in tile flow was not significantly different among treatments in 2011 and was decreased by the treatments of FGD and FGD/C in 1996 (Table 4). Due to the FGD product containing high level of B[8], B concentrations were generally significantly higher for the FGD and FGD/C treatments than SOIL treatment in both 1996 and 2011. Boron concentrations were lower for the FGD/C treatment than FGD treatment in 1996 because B was bound by the compost. Concentration of Fe was decreased at by the FGD and FGD/C treatments in 1996, and concentration of Mn was increased for FGD/C treatment compared to the SOIL treatment in 1996. Mean concentrations of As, Ba and Hg were occasional increased by addition of FGD product (Table 5). Concentrations of Cd, Pb and Se were increased by the treatment of FGD/C in 1996 but not in 2011.

Greenhouse experiment - Algae growth and P concentration in ponded water

FGD gypsum reduced soluble P concentrations and algae growth in ponded water above the soil surface (Fig. 2 and Table 6). This is a win-win situation where the gypsum not only has the ability to increase yields, but also to improve the quality of the environment by reducing P movement to susceptible water bodies.

CONCLUSIONS

Reclamation of acid mine soil using FGD product can be successfully accomplished. Long-term monitoring of runoff and tile flow does not indicate any potential long-term negative impacts associated with the utilization of FGD product. FGD gypsum may be used to improve the environmental quality by reducing eutrophication of lakes and rivers

REFERENCES

[1] Sutton, P., and W.A. Dick. Adv. Agron., 1987, 41:377-405.
[2] Bigham, J.M., D.A. Kost, R.C. Stehouwer, J.H. Beeghly, R. Flowler, S.J. Traina, W.E. Wolfe, and W.A. Dick. Fuel, 2005, 84:1839-1848.
[3] Korcak, R.F. J. Environ. Qual., 1988, 17:469-473.
[4] Stehouwer, R.C., P. Sutton, R.K. Fowler, and W.A. Dick. J. Environ. Qual., 1995, 24:165-174.
[5] Ritchey, K.D., C.M. Feldhake, and R.F. Korcak. 1996. Plant Soil, 1996, 182:209-219.
[6] Chen, L., D. Kost, and W.A. Dick. Soil Sci., 2010, 175 (6):270-277.
[7] **Chen, L.** and W.A. Dick. Gypsum as an Agricultural Amendment: General Use Guidelines. 2011, http://ohioline.osu.edu/b945/b945.pdf.
[8] Chen, L., Y. Tian, R. Stehouwer, D. Kost, X. Guo, J.M. Bigham, J. Beeghly, and W.A. Dick. Fuel, 2013, 162;129-137.
[9] The Ohio State University Extension Service. Ohio Agronomy Guide. Bulletion No. 472 – 12th Edition. 1988, The Ohio State University Extension Service, Columbus, OH.
[10] SAS Institute. SAS/STAT User’s Guide. 2004, SAS Institute Inc, Cary, NC.

Table 1. Concentrations of elements in the sandy soil, clay soil, and flue gas desulfurization (FGD) gypsum.

Element	**Sandy soil**	**Clay soil**	**FGD gypsum**
	-----------------------------	mg kg^{-1} -------------------------------------	
P	514	668	22.1
K	1960	8060	90.4
Ca	2240	4890	170000
Mg	1800	5690	2190
S	241	447	143000
Al	12000	28900	1370
B	<1.52	31.2	10.4
Cu	10.3	28.4	1.88
Fe	11500	21400	2680
Mn	167	120	55.4
Mo	1.39	5.19	1.20
Na	140	233	192
Zn	41.2	80.3	28.5

Table 2. Concentrations of selected constituents in runoff from minesoil reclaimed with SOIL, FGD, and FGD/C in 1996 and 2011.

Treatment	**pH**	**EC**	**Ca**	**S**	**K**	**Mg**	**Al**	**B**	**Fe**	**Mn**
		dS m^{-1}	---------------------------------- mg L^{-1} --							
1996										
SOIL	7.45 b†	0.54 b	67.3 c	65.0 c	4.26 c	20.6 c	0.051 c	0.037 c	0.024	0.032 b
FGD	7.66 a	2.46 a	309 a	0424 a	12.5 a	151 a	0.093 a	1.678 a	0.036	0.103 b
FGD/C	7.59 ab	2.50 a	231 b	0331 b	7.43 b	127 b	0.071 a	0.744 b	0.024	0.634 a
LSD$_{0.05}$	0.17	0.17	21.9	43.5	1.98	24.1	0.018	0.236	0.035	0.233
2011										
SOIL	7.78 a	0.88 c	109 c	119 c	1.42	53.2	<0.031	0.026 c	0.013	0.029
FGD	7.92 a	2.04 a	381 a	356 a	3.44	82.2	<0.031	0.182 a	0.005	0.011
FGD/C	7.52 b	1.69 b	301 b	297 b	2.63	63.8	<0.031	0.136 b	0.004	0.035
LSD$_{0.05}$	0.19	0.25	63	42	4.34	50.7		0.040	0.044	0.096

†Treatments with different letters in the same year are significantly different at the $P \leq 0.05$ level.

Table 3. Selected Resource Conservation and Recovery Act (RCRA)-regulated elements in runoff from minesoil reclaimed with SOIL, FGD, and FGD/C in 1996 and 2011

Treatment	**As**	**Ba**	**Cd**	**Cr**	**Pb**	**Hg**	**Se**
	--			mg L^{-1}	--		
1996							
SOIL	0.024	0.013 a[†]	0.0010	0.0006 b	0.0068	0.0296	0.141
FGD	0.030	0.014 a	0.0011	0.0014 a	0.0104	0.0322	0.163
FGD/C	0.039	0.008 b	0.0010	0.0007 b	0.0127	0.0287	0.202
$LSD_{0.05}$	0.025	0.003	0.0007	0.0007	0.0075	0.0136	0.093
2011							
SOIL	<0.0097	0.038 c	<0.0004	0.0033	<0.0043	ND[‡]	<0.013
FGD	<0.0097	0.063 a	<0.0004	0.0050	<0.0043	ND	<0.013
FGD/C	<0.0097	0.050 b	<0.0004	0.0046	<0.0043	ND	<0.013
$LSD_{0.05}$		0.011		0.0023			

[†] Treatments with different letters in the same year are significantly different at the $P \le 0.05$ level.

[‡] Not determined.

Table 4. Concentrations of selected constituents in tile flow from minesoil reclaimed with SOIL, FGD, and FGD/C in 1996 and 2011.

Treatment	**pH**	**EC**	**Ca**	**S**	**K**	**Mg**	**Al**	**B**	**Fe**	**Mn**
		dS m^{-1}	------------------------------------- mg L^{-1} --							
1996										
SOIL	7.42 b†	1.91 b	371 b	917 c	8.58 c	384 b	11.1 a	0.20 c	9.61 a	150 b
FGD	7.78 a	5.92 a	420 a	1330 b	23.9 a	816 a	0.22 c	2.12 a	0.09 b	144 b
FGD/C	7.54 b	4.01 ab	412 a	1440 a	15.2 b	830 a	3.73 b	0.82 b	0.91 b	201 a
LSD$_{0.05}$	0.18	2.39	16.0	60.4	1.85	43.3	2.34	0.24	4.29	12.9
2011										
SOIL	5.92	1.48 b	182 c	278	2.87	90.0	0.58	0.05 b	18.7	15.7
FGD	6.17	2.37 a	432 a	453	4.01	110	0.79	0.20 a	0.04	6.80
FGD/C	5.85	2.14 ab	365 b	426	3.78	104	0.79	0.14 ab	4.13	11.2
LSD$_{0.05}$	1.38	0.82	24	205	3.03	103	1.21	0.09	65.0	30.3

† Treatments with different letters in the same year are significantly different at the $P \le 0.05$ level.

Table 4. Selected Resource Conservation and Recovery Act (RCRA)-regulated elements in tile flow from minesoil reclaimed with SOIL, FGD, and FGD/C in 1996 and 2011.

Treatment	**As**	**Ba**	**Cd**	**Cr**	**Pb**	**Hg**	**Se**
	-- mg L^{-1} --						
1996							
SOIL	0.002 b[†]	0.014	0.0039 b	0.020 b	0.044 b	0.0055 b	0.175 b
FGD	0.017 a	0.016	0.0025 c	0.019 b	0.044 b	0.0158 a	0.201 b
FGD/C	0.010 ab	0.015	0.0055 a	0.027 a	0.060 a	0.0080 b	0.371 a
$\text{LSD}_{0.05}$	0.011	0.002	0.0007	0.002	0.008	0.0065	0.103
2011							
SOIL	<0.0097	0.027 c	0.0010	0.013	<0.0043	ND[‡]	<0.013
FGD	<0.0097	0.054 a	0.0008	0.010	<0.0043	ND	<0.013
FGD/C	<0.0097	0.047 b	0.0007	0.011	<0.0043	ND	<0.013
$\text{LSD}_{0.05}$		0.001	0.0030	0.019			

[†] Treatments with different letters in the same year are significantly different at the $P \leq 0.05$ level.

[‡] Not determined.

Table 5. Soluble P concentration in ponding water as affected by gypsum and soybean cultivars.

Soil type	Soybean cultivar	3360 kg ha^{-1} gypsum	No gypsum
		------------------------mg L^{-1}	------------------------------
Sandy soil	Wooster	1.35	2.48
	Wyandot	1.48	1.74
Clay soil	Wooster	0	0.01
	Wyandot	0	0.20

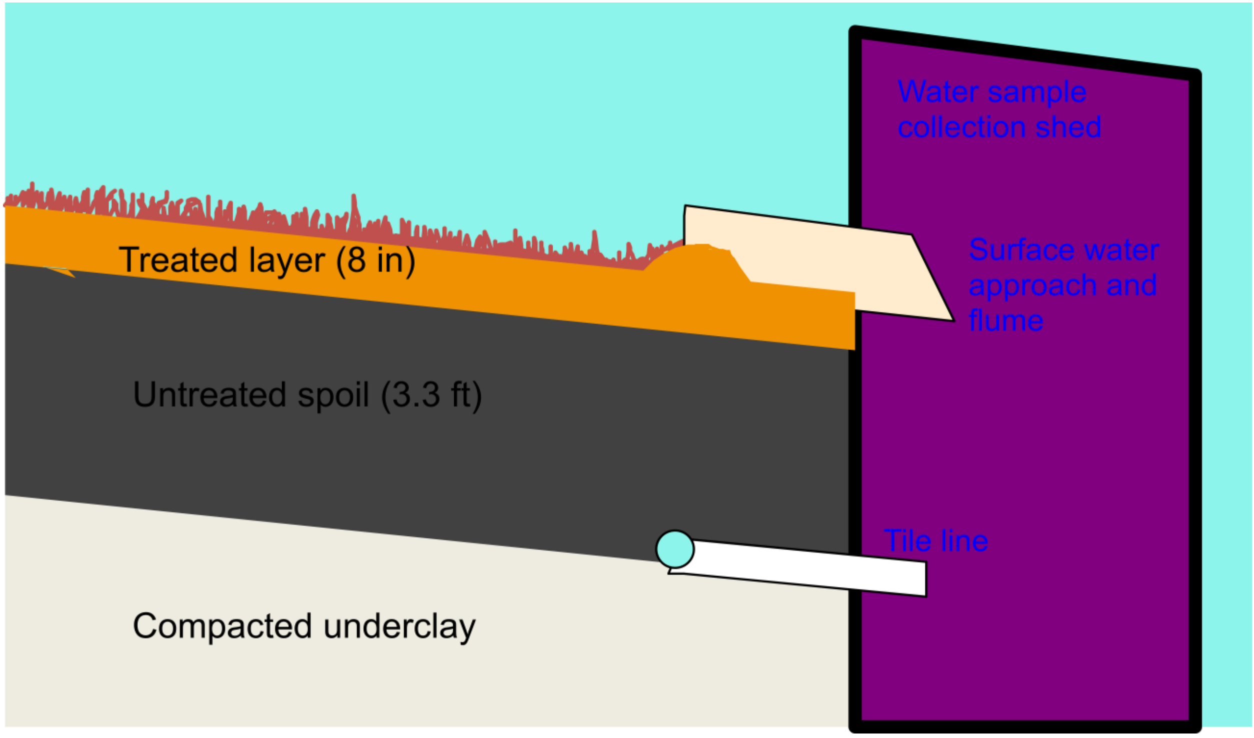

Fig. 1. Facility for runoff and tile flow sampling.

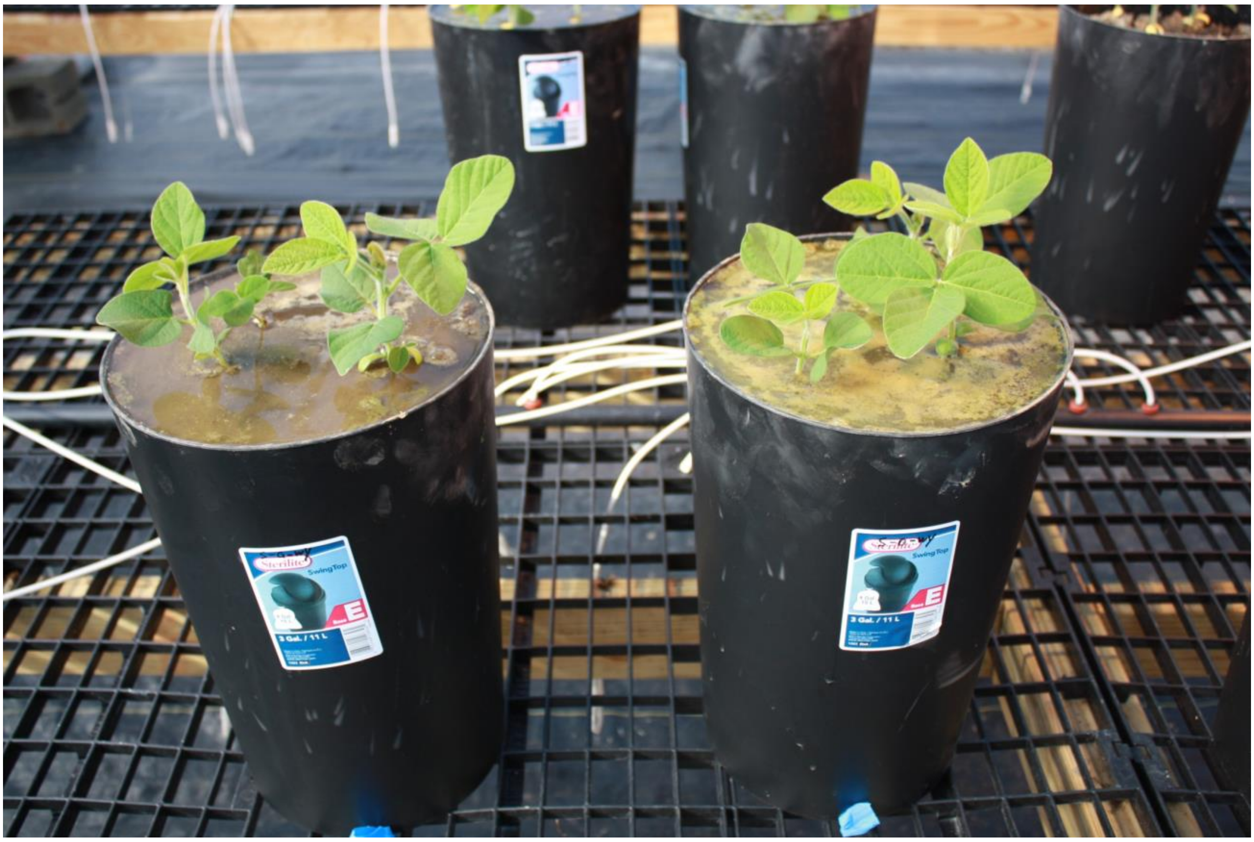

Fig. 2. FGD gypsum reduced algae growth. Soil treated with gypsum (left pot) and soil not treated with gypsum (right pot).