IPL/Gypsoil/IUPUI
Gypsum study at Britton Farms

Abstract:

The impact of gypsum amendment on soluble reactive phosphorus (SRP) export from agricultural fields, and soil chemical properties was investigated at two adjacent fields in the Walnut Creek watershed (IN). The fields supported a corn (*Zea mays*, L) crop during the monitoring period (April 2014 - April 2015) and were similarly managed, except that one field was treated with FGD (1 ton $acre^{-1}$) and the other was not. Results showed significantly ($P<0.04$) lower SRP concentration (41% lower) during the growing season (May - early July) in tile waters from the FGD-treated field compared to the untreated field (control). Reduction in concentration (14-17%) was also measured during the pre-plant (April-May) and post-harvest (November- January) periods, but difference was only marginally significant. With exception of calcium and sulfate (1.3 and 3 times higher respectively in treated field), tile waters composition was similar with regard to nitrate and other water chemistry parameters (Mg, Na, pH, EC). The concentration of water-extractable P (an index of P export) was 1.5 times higher in soils from the untreated compared to the FGD-treated field. In the latter field, plant available P (Olsen test) was highest in the 20-30 cm soil depth range, whereas in the untreated field available P was highest in the surface layer (0-5) where it is most susceptible to loss in runoff. Results also showed a trend toward higher levels (although not significant) of labile organic carbon (microbial biomass, soil respiration) and cation exchange capacity (CEC) in the FGD-treated field compared to the control. These results indicate that even a one-time application of FGD can have measurable effects on soil properties known to be linked to nutrient cycling, soil fertility and soil health. It is unclear for how long this impact would last and how often FGD application needs be made to maintain these positive effects.

Introduction:

FGD (flue gas desulfurization) Gypsum:

FGD gypsum ($CaSO_4$•$2H_2O$) is produced by power utilities in limestone-forced oxidation scrubbers that remove sulfur dioxide from the flue gas stream after coal combustion. In general, limestone-forced oxidation exposes the flue gas to limestone slurry, initially forming calcium sulfite. Forcing additional air into the system oxidizes the calcium sulfite and converts it into gypsum (calcium sulfate, $CaSO_4$). Fly ash is removed prior to the limestone-forced oxidation system, resulting in a relatively pure gypsum product. Processing of the gypsum may include centrifugation for initial dewatering and fines removal, followed by further dewatering, and sometimes washing to further remove soluble constituents. The gypsum that is recovered is high quality and suitable for agricultural uses. However, FGD gypsum production currently exceeds demand by a considerable margin. In 2010, 22 million tons of FGD gypsum was produced but only 10.7 million tons was used, mostly for wallboard production (ACAA, 2012). The remaining material must be disposed of, usually at some cost to the utilities that produce it and to the environment in the form of extra landfilling.

Mobility of Agricultural Nutrients (Phosphorus, Nitrogen) and Water Quality:

The export of nutrients from agricultural fields contributes to water pollution with deleterious impact on human and aquatic ecosystems health. Nitrogen and phosphorus are essential to maintaining agricultural productivity and food security, but can trigger a host of water quality deterioration when they enter our lakes and rivers. Nitrate is a regulated water pollutant. The US Environmental Protection Agency (EPA) has established a maximum concentration limit of 10 mg N L^{-1} for nitrate in drinking water. This limit is often exceeded in rivers and streams, especially after rainfall events following fertilizer application to crop fields. Phosphorus is a primary limiting nutrient for a variety of terrestrial plants and a major trigger of algal blooms in aquatic ecosystems. In modern agricultural systems, a significant portion of the phosphorus applied to fields to support higher crop yields (typically in the form of fertilizers or animal manure) is often transported off the fields and into waterways, where it becomes available to aquatic organisms. Under normal or “natural” circumstances, the concentration of available phosphorus (soluble reactive P, SRP) in aquatic systems limits the growth of certain organisms, primarily algae. Freed from the constraints of limited phosphorus in freshwater systems, algal “blooms,” rapid increases in the growth and density of algae populations, can occur. The increasing frequency of algal blooms in the United States and elsewhere have made nutrient management a high priority in many areas due to the problems associated with them. Decomposition of algal biomass by resident microbes leads to depletion of dissolved oxygen (DO), ultimately resulting in hypoxia and enhanced potential for fish kills. The so-called dead zone (dissolved oxygen < 2 mg L^{-1}) in the Gulf of Mexico is one of the best known hypoxic zones in the world. Its size has doubled during the last decade (1993 - 2006). Direct economic impacts can be felt as a result of excessive algae, including loss of tourism and recreation income due to degraded waters, reduced fishery revenues, and higher water treatment costs for drinking water utilities to mitigate toxins released by some algal species. Human health concerns include the effects of exposure to waterborne toxins via skin contact or ingestion. Harmful environmental effects are seen in the disruption of natural systems and the loss of biodiversity due to hypoxia. Although the effects of high nutrient loads are being observed in freshwater and estuarine systems across the country, intensive agriculture in the Corn Belt States (including Indiana) poses the greatest threat to water quality and ecosystem health in the Mississippi River delta due in part to its high percentage of total area (about 60 %) under cultivation.

Naturally, in response to these impacts many local, state, regional and national agencies and stakeholders have made nutrient management from both point and non-point sources a priority. Possible approaches range from tightening controls on the types, amounts, and times at which fertilizers can be applied to fields to various treatment and filtration technologies. The ideal solution would be one or a suite of tools and practices that, at reasonable costs, will allow farmers to support their livelihood while acting as responsible stewards of the lands and waters their farms impact.

Gypsum Effects on Agricultural Phosphorus:

The amendment of soils with FGD has been identified as an excellent market for FGD gypsum, but this potential has not been fully exploited. FGD gypsum has been shown to boost yields for some crops while reducing fertilizer requirements. More recently, preliminary studies have shown gypsum can reduce the export of soluble reactive phosphorus (SRP) from croplands by 40 -70 percent. Because it is readily available to living organisms, SRP is the most problematic form of P that can enter rivers and lakes. This provides additional incentive for applications in areas of the Midwest impacted by excess phosphorus in surface water bodies.

This research was a field demonstration in the Big Walnut Creek in Indiana of the potential for addressing both the issue of surplus FGD gypsum and excessive agricultural phosphorus loading to surface waters.

Research

Summary of activity:

Two adjacent cultivated fields draining into the Walnut Creek were selected for the study (Fig. 1). The fields are located just west of North Salem (IN) at the border between Hendricks and Putnam counties. The landowner maintains an extensive record of the tile layout across the fields, as well as their land-use/management history. The fields are similarly managed (identical crop rotation, fertilizer, and other practices), and have never been treated with FGD in the past. One field (red area in Fig. 1) was treated with FGD on March 31, 2014 at a rate of 1 ton acre^{-1} (2.24 ton ha^{-1}), while the other was not treated (serving as control). The fields have been under a no-till corn-soybean (*Glycine max*, L.) rotation, with corn being the crop grown during the 2014 growing season. At the time of planting on May 6, 2014, startup fertilizer was applied (60 pound acre-1 of 28 % N fertilizer, 25 pound acre^{-1} of 10-34-0 granular fertilizer). Corn was side-dressed with additional N fertilizer during the last week of May.

Water samples were collected at the outlet of an 8” pipe from the FGD-treated field. For the non-treated field, two 6” diameter tiles were selected to ensure that at least one tile would be available for water sampling. Water samples were collected beginning March 25, 2014 and ending April 24, 2015. Water samples were collected in acid-washed polypropylene bottles, stored temporarily in a freezer by the farm manager, and transported to the laboratory for analysis. Samples were filtered and stored frozen until analyzed.

Soil samples were also collected in April 2014 (beginning of experiment) and in November 2014. At each field, soil samples (0-30 cm) were collected along a catena (topslope to downslope). A total of 32 soil samples were collected during each sampling event. Soil samples were air-dried, sieved, and used for determination of basic soil chemical properties and residual plant nutrients. A portion of the samples collected in November was kept field-moist and used for determination of soil biochemical properties.

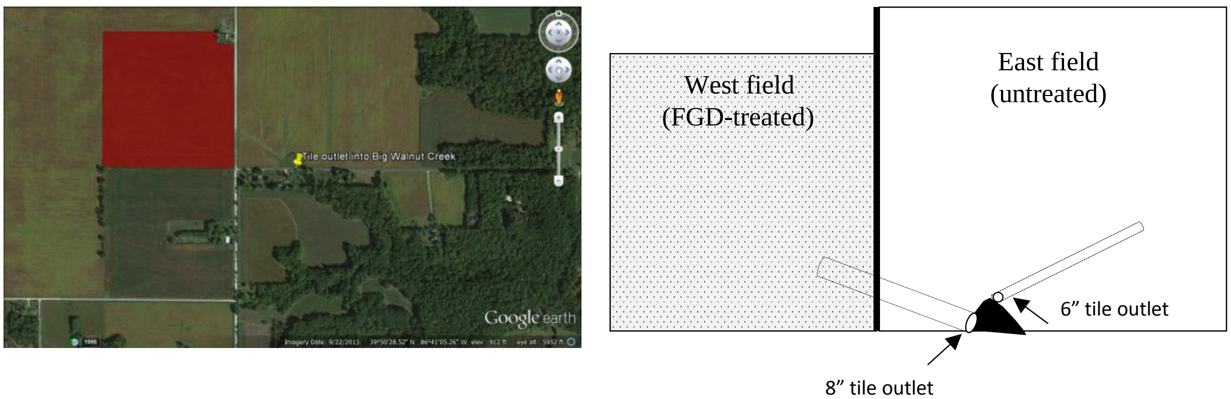


Figure 1. Location of the study sites at Britton Farms, along the Putnam-Hendricks County (Indiana) border. The west field (area in red on air photo, about 40 acres) was treated with FGD; the east field (across the road) was not treated and served as control. Water samples were collected at the tiles outlet near a depression (shown in black).

Analytical methods:

Water samples were analyzed for the following constituents and parameters:

- SRP: Analysis was carried out using EPA method 365.3 on an Aquachem Konelab 20 photometric analyzer.
- Nitrate: Analysis was carried out using EPA method 353.1 on an Aquachem Konelab 20 photometric analyzer.
- Sulfate: Analysis was carried out using EPA method 375.4 on an Aquachem Konelab 20 photometric analyzer.
- Dissolved cations (calcium, magnesium, potassium, sodium) using inductively coupled plasma spectrometer.

Soil samples were analyzed for the following parameters:

- pH: electrometrically using a pH-meter (1:2 soil to water suspension)
- Electrical conductivity using a conductivity-meter and a 1:5 soil-water suspension.
- Cation exchange capacity: Extraction of soil with ammonium acetate (1 N) and analysis of exchangeable bases (Ca, Mg, K, Na) in filtrate using inductively coupled plasma atomic emission spectrometry. Exchangeable acidity in filtrate was determined by titration with NaOH (0.1 N) with phenolphthalein as color indicator.
- Water soluble P: extraction of air-dried soil samples with deionized water (16 h) and analysis of SRP using EPA method 365.3.
- Bicarbonate extractable P (Olsen P): Soil extracts were analyzed for SRP NaHCO3 (1 M) and analysis of SRP using EPA methods 365.3 on an Aquachem Konelab 20 photometric analyzer.
- Total P: combustion of soil samples in a furnace (550 ^{o}C, 1 h) and acid (1 N HCl) extraction of ash. Extract was diluted and analyzed for SRP as described above.
- Soil respiration: incubation of field-moist soil in a jar and determination of carbon dioxide (CO_2) production over time using a Varian CP-3800 gas chromatograph.
- Microbial biomass carbon: by the substrate-induced respiration method, involving amendment of field-moist soil with glucose and determination of the short-term (4 h) enhancement in CO_2 production.
- Organic carbon and nitrogen: by dry combustion (950°C) of ground (150 μm) soil samples on a Vario Cube CN analyzer.

Results:

The amount of rainfall (1,079 mm) during the monitoring period (April 2014-April 2015) was near the long-term average for the region (1,040 mm). As typical of the central US Midwest, tile flow occurred between November and January and then March to June, with almost no flow from mid to late summer. Therefore, no data are available for the summer months. Consistent with these hydro-climatic patterns and farming practices calendar, the data are summarized in this report as: pre-plant (April-May), growing season (May-early July), and post-harvest (November-February).

Agricultural nutrients concentration in tile waters

During the monitoring period, nitrate concentration in tile waters ranged between 1.6 and 16.8 mg N L^{-1} (Figs. 2a and 3a), with 7% of the samples exceeding the EPA maximum concentration limit of 10 mg N L^{-1} in drinking water. Temporal variation in nitrate concentration was not affected by the FGD treatment, but by weather events and timing of fertilizer application. The highest nitrate concentrations were observed in June 2014 following side-dressing of corn with N fertilizer. Compared to the growing season, nitrate concentration in tile waters was 1.3 times lower during the period November 2014 to April 2014 (dormant season, Figs. 2a, 3a, and 4a).

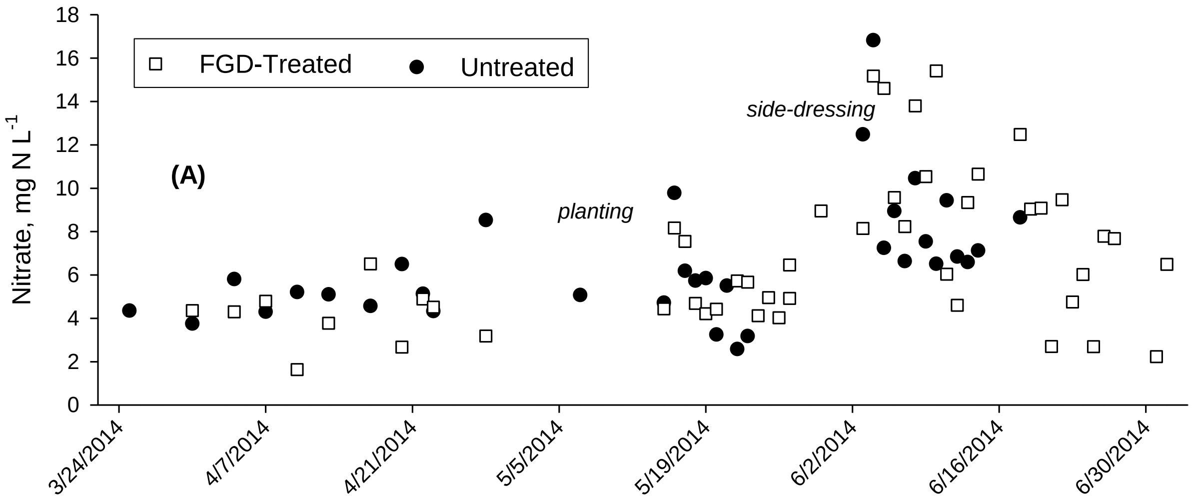
In contrast to nitrate, variability in SRP concentration probably reflected the effect of FGD treatment and plant growth. During the pre-plant period, SRP concentration was generally similar in tile waters from the treated and untreated fields (Fig. 2b). Following fertilizer application to corn, a few spikes in SRP concentration were observed in June-July, but the increase in concentration was much greater in the control compared to the FGD-treated field. Mean SRP concentration during that period (fig. 4) was significantly lower (as determined by t-test) in tile waters from the FGD-treated (17.6 µg P L^{-1}) compared to the control (30.05 µg P L^{-1}). That corresponded to a 41% reduction in SRP concentration. Following the harvest of corn, a marked increase in SRP concentration was noted, probably due to the absence of vegetation P uptake and increased leaching (Fig. 3b). SRP concentration in waters from the FGD treated field was still lower (53.1 vs 63.9 µg P L^{-1}), but the difference was only marginally significant ($P<0.05$).

Besides N and P, the chemical composition of tile waters was also monitored. For most parameters, the chemical composition of drainage water from the control and FGD-treated field was nearly identical (Table 1). However, the concentration of calcium and sulfate was noticeably higher (1.2 and 3 times, respectively) in drainage waters from the FGD field. This is not surprising since Ca and SO_4 are the main constituents of most FGD materials. Elevated concentration of sulfate in drinking water has been linked to diarrhea and other abdominal complaints in some sub-populations. The EPA has established a secondary maximum concentration limit of 250 mg L^{-1}. Sulfate concentration (range: 86.4 - 201.8 mg L^{-1}) in tile waters from the FGD-treated field never reached that threshold value.

Table 1. Chemical composition of tile water from untreated (control) and FGD-treated fields during the period March – June 2014. Values are mean standard error (n=12).

	Treatment	
	Control	FGD
pH	7.86 (0.09)	7.62 (0.08)
Electrical conductivity, mmho cm^{-1}	0.42 (0.04)	0.46 (0.03)
Calcium, mg L^{-1}	22.54 (2.10)	27.01 (2.06)
Magnesium, mg L^{-1}	24.54 (1.83)	19.51 (1.31)
Sodium, mg L^{-1}	3.64 (0.18)	3.50 (0.18)
Potassium, mg L^{-1}	1.75 (0.04)	1.71 (0.04)
Sulfate†, mg L^{-1}	44.7 (3.7)	141.4 (3.7)

†Data are for the period November 2014 to April 2015. N = 20-44 observations.



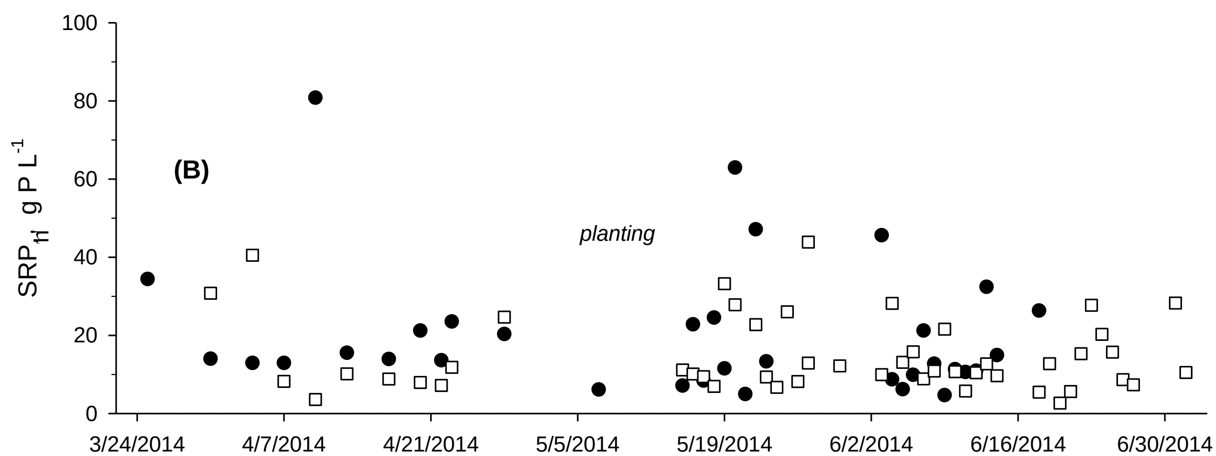
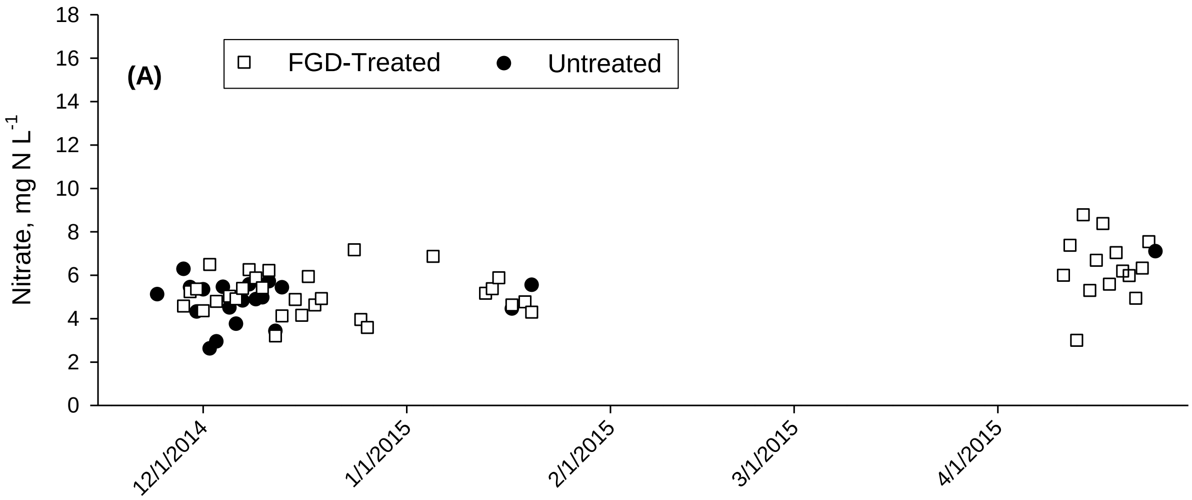


Fig. 2. Temporal variation in nitrate (A) and soluble reactive P (B) concentration in tile waters from FGD-treated and untreated fields during the pre-plant and early growing season.



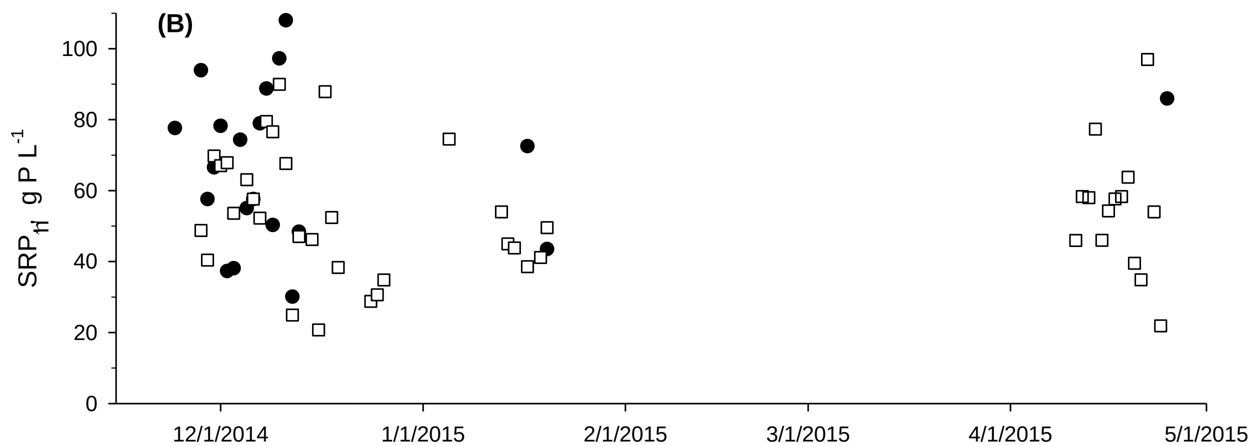


Fig. 3. Temporal variation in nitrate (A) and soluble reactive P (B) concentration in tile waters from FGD-treated and untreated fields during the post-harvest period (November - February).

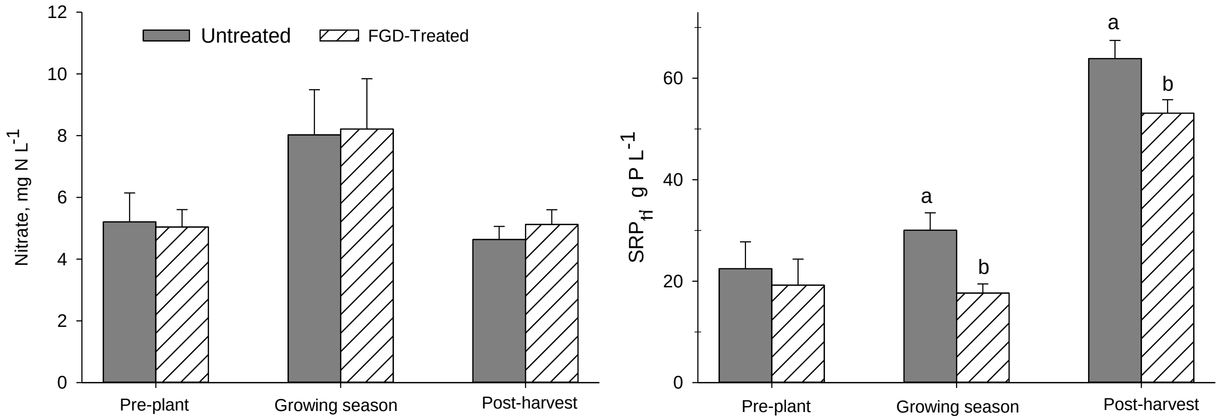


Fig. 4. Seasonal average concentration of nitrate and soluble reactive P (SRP) in tile waters from FGD-treated and untreated fields during the pre-plant (April-May), early growing season (May-early July) and post-harvest period (November-February). Different letters above adjacent bars indicate significant difference ($P < 0.05$) between the treatment and control.

Chemical and biochemical properties of soils

Soil pH at the study sites ranged between 6.1 and 7.2 and no effect of FGD application on soil pH was noted (Table 2). Electrical conductivity ranged between 0.04 to 0.22 mmho cm^{-1} (Table 2) with higher level in the FGD-treated field compared to the control. This range is well below the level (1 mmho cm^{-1}) where salinity could become limiting to plant growth. However, that is a factor to monitor if frequent applications of FGD were to be made.

There was no effect of FGD application on total soil P, water extractable and plant available P (as determined by the Olsen test). However, it is important to note the lower (1.7 times) levels of water-extractable P in the surface layers (0-10 cm) of the FGD-treated field (Table 3). Water extractable P can be a strong predictor of P export from agricultural fields. In the FGD-treated field, the concentration of plant available P increases with soil depth, whereas in the untreated field concentration was highest near the soil surface (0-5) where P is most susceptible to loss in runoff.

There was no significant difference between the untreated and FGD-treated fields with respect to total soil organic carbon and labile carbon concentration (Table 4). However, it is important to note that both microbial biomass carbon (a measure of the total soil microbial population) and soil respiration (a measure of the quality of organic C to sustain the activity of soil microbes) were numerically higher in the FGD-treated field (Table 4). These are biochemical attributes often linked to soil health and they often respond quickly to change in land management. If maintained, it is likely that a significant effect of the FGD treatment could be detected within the next few years.

FGD application has noticeable effect on cation exchange capacity (CEC) and the availability of bases on the soil exchange complex (Table 2; Fig. 5). In the untreated field, the concentration of nutrient cations (Ca, Mg) decreased between April and November, probably due to plant uptake and leaching (Fig. 5). In contrast, increase in concentration was observed throughout the soil profile in the FGD-treated field. At the end of the first growing season, CEC averaged 20.5 and 24.9 $cmol_c\ kg^{-1}$ in the untreated and FGD-treated fields, respectively (Table 2). Corresponding values for base saturation was 78 and 84 %, respectively. The rapid effect of FGD on the soil exchange complex is noteworthy as it indicates a clear improvement in the ability of soils to retain nutrients with only one FGD application.

Table 2. Chemical properties of soils in a cultivated field treated with gypsum-FGD and in an adjacent untreated field. Soil samples were collected in November 2014, 8 months after application of FGD. Values are mean with standard deviation in parentheses.

	Depth, cm	Treatments: Untreated	Treatments: FGD-treated
pH	0 - 5	7.2 (0.5)	7 (0.5)
	5 - 10	7.1 (0.3)	7.1 (0.6)
	10 - 20	7 (0.3)	6.7 (0.9)
	20 - 30	6.9 (0.2)	6.1 (0.4)
Electrical conductivity, mmho cm^{-1}	0 - 5	0.09 (0.12)	0.22 (0.05)
	5 - 10	0.07 (0.07)	0.07 (0.09)
	10 - 20	0.05 (0.05)	0.18 (0.05)
	20 - 30	0.04 (0.01)	0.12 (0.04)
Cation exchange capacity, $cmol_c\ kg^{-1}$	0 - 5	20.1 (3.5)	27.5 (9.6)
	5 - 10	19.8 (6.2)	22.9 (5.5)
	10 - 20	19.0 (7.9)	28 (5.3)
	20 - 30	23.3 (9.5)	21.5 (8.5)
% base saturation	0 - 5	79	85
	5 - 10	79	83
	10 - 20	76	87
	20 - 30	81	84

Table 3. Phosphorus concentration in a cultivated field treated with gypsum-FGD and in an adjacent untreated field. Soil samples were collected in November 2014, 8 months after application of FGD. Values are mean with standard deviation in parentheses.

		Treatments	
	Depth, cm	Untreated	FGD-treated
Water extractable P, mg P kg^{-1}	0 - 5	5.4 (3.5)	3 (2.7)
	5 - 10	3.5 (0.1)	2.2 (2.1)
	10 - 20	1.8 (0.7)	1.5 (1)
	20 - 30	1.1 (0.2)	0.9 (0.6)
Bicarbonate extractable P, mg P kg^{-1}	0 - 5	10.7 (3.79)	9.35 (4.76)
	5 - 10	7.61 (3.64)	9.2 (5.48)
	10 - 20	6.89 (3.59)	7.45 (4.37)
	20 - 30	5.81 (0.32)	11.22 (5)
Total P, mg P kg^{-1}	0 - 5	350.8 (86.1)	402.2 (10.4)
	5 - 10	381.6 (29.7)	386.1 (90.1)
	10 - 20	308.8 (63)	389.7 (36.3)
	20 - 30	343.4 (53.8)	385.4 (101)

Table 4. Total and labile soil organic carbon in soils in a cultivated field treated with gypsum-FGD and in an adjacent untreated field. Soil samples were collected in November 2014, 8 months after application of FGD. Values are mean with standard deviation in parentheses.

		Treatments	
	Depth, cm	Untreated	FGD-treated
Soil organic carbon, %	0 - 5	1.99 (0.2)	1.8 (0.4)
	5 - 10	1.8 (0.05)	1.58 (0.47)
	10 - 20	1.63 (0.26)	1.2 (0.78)
	20 - 30	1.45 (0.01)	1.13 (0.37)
Total soil nitrogen, %	0 - 5	0.18 (0.01)	0.14 (0.07)
	5 - 10	0.15 (0.04)	0.17 (0)
	10 - 20	0.14 (0.01)	0.11 (0.06)
	20 - 30	0.14 (0.02)	0.12 (0.02)
C to N ratio	0 - 5	11.3	13
	5 - 10	12.3	9.3
	10 - 20	11.5	10.5
	20 - 30	10.4	9.2
Microbial biomass carbon, mg C kg^{-1}	0 - 5	387.4 (128.9)	501.3 (198.5)
	5 - 10	210 (67.4)	354.8 (169.9)
	10 - 20	211.4 (22.6)	216.7 (70.4)
	20 - 30	119.3 (27.9)	159 (30.3)
Soil respiration, mg CO_2-C kg^{-1} soil day^{-1}	0 - 5	14 (3.3)	16.1 (3)
	5 - 10	8.9 (1.6)	8.7 (3.2)
	10 - 20	6.1 (1.2)	6.3 (2.3)
	20 - 30	5.1 (0.6)	4.9 (0.9)

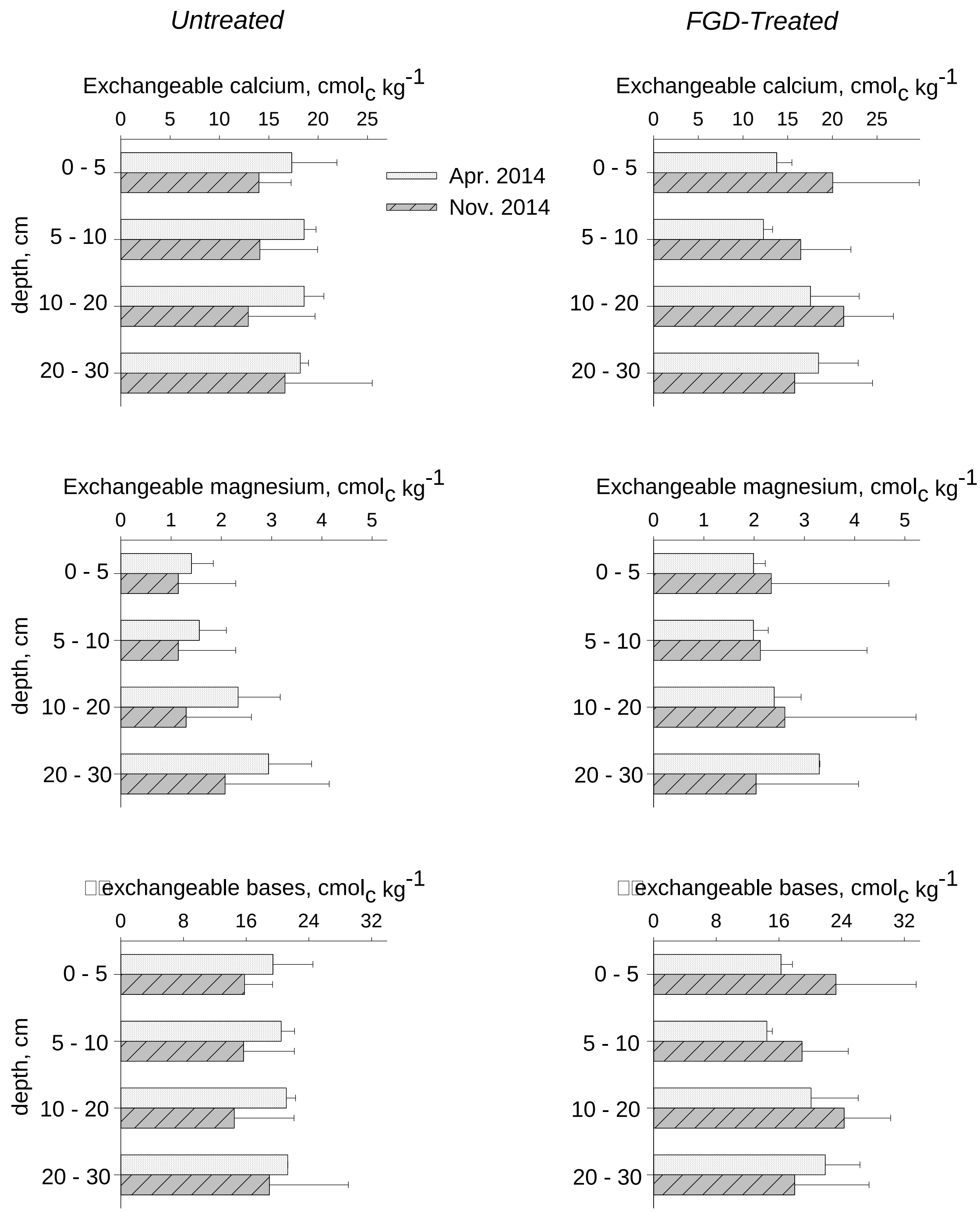


Fig. 5. Concentration of exchangeable bases in the plow layer of a field treated with gypsum-FGD and in an adjacent untreated field. Soil samples were collected in April 2014 at the time of FGD application (white bar) and after harvest in November 2014 (gray bar). Results are depicted as mean with error bars indicating ± standard deviation. Note cmol$_c$/kg = meq/100 g.

Acknowledgment

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