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Effects of Fluidized Gas Desulfurization (FGD) Gypsum on Non-Target Freshwater and Sediment Dwelling Organisms

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Abstract Fluidized gas desulfurization gypsum is a popular agricultural soil amendment used to increase calcium and sulfur contents, and reduce aluminum toxicity. Due to its surface application in conservation tillage systems and high solubility, the soluble components of gypsum may be transferred with agricultural runoff into receiving waters. The current study measured toxicity of gypsum to *Ceriodaphnia dubia*, *Pimephales promelas, Chironomus dilutus,* and *Hyalella azteca*. Solutions at 2,400 mg gypsum/L (maximum solubility) produced no observable toxicity to *C. dubia* and *P. promelas.* Mixtures of a control sediment and gypsum indicated no observed toxicity effects for *H. azteca*, although effects were noted at 25% dilution for *C. dilutus*. Data suggest gypsum is not harmful to freshwater organisms at concentrations expected in the agricultural environment.

Keywords Soil amendment · Toxicity · Macroinvertebrate

Gypsum ($CaSO_4 \cdot 2H_2O$) is both a naturally occurring mineral and a byproduct of the fluidized gas desulfurization (FGD) process used in coal-fired power plants to reduce sulfur emissions. This synthetic gypsum is typically more pure than the naturally occurring, mined forms, and has a nearly consistent particle diameter of 50 µm (USDA 2006). According to the USEPA (2008) FGD production in the United States during 2006 was approximately 12.2 billion kg, with 2% being used in agricultural settings. By 2008, 1.1 billion kg of gypsum were used for agricultural purposes (USGS 2009). These purposes include serving as a (1) nutrient source for plants; (2) soil conditioner to improve physical and chemical properties; or (3) means for reduction of contaminant (nutrient, sediment, pesticide) transport to receiving waters (USEPA 2008). Typical agricultural soil application rates for gypsum range from 2,500 to 5,000 kg/ha (USDA 2006).

Historically, gypsum is the primary amendment used to remediate soils with excessively high sodium concentrations that impede plant growth and contribute to dispersive soil conditions. This is accomplished by the dissolution of gypsum, and its resultant increase in soil electrolyte concentrations, particularly calcium, which replaces sodium adsorbed on the soil complex. This effect leads to reduced dispersion and increased aggregation of soils (USDA 1954). After a 2.54 cm rainfall, gypsum reacts with rainwater, dissolving at a rate of 534 kg/ha (USDA 2006). Converting readily soluble phosphorus (P) into less soluble forms, gypsum is able to reduce nutrient runoff into receiving water bodies (USEPA 2008). If aluminum ions are present in the soil, they may be displaced by sulfur provided by gypsum, in order to decrease effects of soil acidity.

The objectives of this study were to determine acute (48 h) and chronic (7–10 days) effects of a synthetic gypsum solution on the fathead minnow (*Pimephales promelas*), non-biting midge (*Chironomus dilutus*), scud (*Hyalella azteca*), and water flea (*Ceriodaphnia dubia*).

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Materials and Methods

An industrial source of FGD gypsum (as powder) was obtained from the Southern Company's Newnan, Georgia, plant to utilize in this research. By dissolving 2.4 g of gypsum into 1 L of Milli-Q™ water, a stock solution was made and subsequently used to perform serial dilutions for toxicity assessment concentrations (Table 1). Serial dilutions were completed with the addition of moderately hard reconstituted (MHR) laboratory water (USEPA 2002a). Concentrations were analyzed for the presence of calcium using inductively coupled plasma – atomic emission spectrometry according to USEPA method 200.7 (USEPA 2001). Sulfate concentrations were determined with ion chromatography using USEPA method 300.0/9056A (USEPA 1996).

Organisms used in toxicity assessments were cultured and maintained at the Arkansas State University Ecotoxicology Research Facility (ASU ERF). All test procedures and conditions followed methods outlined by the USEPA (2002a, b). Toxicity assessments were conducted at 25 ± 1°C under a 16:8 light:dark photoperiod. Water chemistry parameters including pH, temperature, dissolved oxygen (DO), conductivity, alkalinity, and hardness were measured when water was initially prepared and after it was removed for daily renewal or test termination. Short term (48 h) toxicity assessments for survival were conducted for *Ceriodaphnia dubia* (water flea) and *Pimephales promelas* (fathead minnow). Longer term (7 days) assessments were also conducted for *C. dubia* (survival and reproduction). In addition, *Chironomus dilutus* and *Hyalella azteca*, two sediment dwelling organisms, were assessed for survival and growth in 10 days assessments.

C. dubia (<24 h old) were exposed to a control solution and five FGD gypsum concentrations (0.15, 0.30, 0.60, 1.2, and 2.4 g/L) using ten replicates for each treatment (15 mL solution in each container). In the 48 h assessments, the final concentration (2.4 g/L) was replicated with one dilution using MHR water and the other Milli-Q™ water, to eliminate the possibility of cation overload due to MHR water. With no observed differences between dilution water sources, the replicate Milli-Q™ water concentration was dropped from subsequent toxicity assessments. Water was renewed daily for 7 days assessments with dilutions from a stock solution, and survival and reproduction were recorded. Organisms were then transferred into renewed water containing food (1 mL of a yeast/trout chow mixture and one drop of *Selenastrum capricornutum*). Values for toxicity assessment endpoints were obtained using a hypothesis test approach with Fisher's Exact Test, Dunnett's Procedure, or Steel's Many-one Rank test. Tests for normality and homogeneity of variance included Shapiro–Wilks and Bartlett's tests, respectively (USEPA 2002b). All statistical comparisons utilized an alpha level of 0.05.

Ten *P. promelas* (<24 h old) were placed in each of four replicate acid-washed test containers per concentration and filled with approximately 100 mL of FGD gypsum-water solution. Statistical procedures utilized were similar to those used with *C. dubia*.

For *C. dilutus* and *H. azteca* assessments, FGD gypsum from the same source as water assessments was mixed with control sediment (Moore et al. 1996) and added to the 100 mL mark in 250 mL wide mouth borosilicate glass beakers. Dilution percentages for *C. dilutus* were 0.01:99.99, 0.1:99.9, 1:99, 10:90, and 25:75, while dilutions for *H. azteca* were 0.1:99.9, 1:99, 10:90, 25:27, and 50:50. Overlying dechlorinated water (Jonesboro, AR municipal water processed through a charcoal filter system) was added to fill the remainder of the beaker. Ten third instar larval midges (13–15 days) were added to each replicate (four replicates at each concentration). To limit stress, organisms were left in their casing (unbleached paper towels). In separate beakers, ten *H. azteca* were added to each of four replicates per FGD gypsum concentration. After 24 h, air was bubbled in each beaker to maintain DO levels. Water was renewed daily throughout test duration. Organisms in each test chamber were fed 1 mL of Tetramin® solution (4 g/L) daily during the 10 days. Overlying water chemistry was assessed with temperature, conductivity, pH, alkalinity, hardness, and ammonia concentrations measured at the beginning (day 0) and end (day 9) of each test. Surviving *C. dilutus* and *H. azteca* were collected from their respective beakers after 10 days, placed in aluminum weigh pans, dried, and assessed for changes in growth. Toxicity assay results were analyzed statistically using Toxcal® (version 5.0.25). Normality assumptions were tested using Shapiro-Wilk's test and Steel's Many-One Rank test to compare variation in survival among sites ($\alpha = 0.05$).

Table 1 Measured FGD gypsum (as calcium and sulfate) concentrations used in toxicity assessments

Concentration (g/L)	Calcium (mg/L)	Sulfate (mg/L)
0.0	17.2	52.7
0.15	53.9	117
0.30	83.6	160
0.60	141	196
1.2	231	331
2.4	576	744

Results and Discussion

Survival of *C. dubia* was not impaired at any concentration of FGD gypsum during 48 h assessments. All

Table 2 10 days toxicity and impairment assessments for *Chironomus dilutus* and *Hyalella azteca*

Organism	Dilution (%) gypsum:sediment	Survival (%)	Mean replicate mass[a] (mg)
Hyalella azteca	0:100 (Control)	98	0.14 ± 0.01
	0.1:99.9	100	0.15 ± 0.01
	1:99	95	0.17 ± 0.01
	10:90	100	0.20 ± 0.01
	25:75	98	0.23 ± 0.02
	50:50	83	0.18 ± 0.02
Chironomus dilutus	0:100 (Control)	100	3.76 ± 0.13
	0.01:99.99	100	3.26 ± 0.13
	0.1:99.9	100	3.40 ± 0.21
	1:99	100	3.59 ± 0.20
	10:90	98	3.35 ± 0.22
	25:75	100	2.90 ± 0.07[b]

[a] Mean replicate mass ± standard error

[b] Statistically significant from control

concentrations demonstrated 100% survival. Mount et al. (1997) reported *C. dubia* 48 h LC_{50} values for $CaSO_4$ (gypsum) to be >1.91 g/L, which complements current study results. When *C. dubia* were exposed to the same gypsum concentrations for 10 days, survival was still unimpaired; however, reproduction was significantly reduced at the 0.0006 and 0.0024 g/L concentrations. The calculated 10 days *C. dubia* reproduction inhibition concentration (IC_{50}) for gypsum was 1.77 g/L with 95% confidence limits of 1.40–2.05 g/L.

As with *C. dubia*, no impairment of survival was noted in any exposed *P. promelas* concentrations during 48 h exposures. Survival at all concentrations ranged from 98 to 100%. Earlier assessments conducted by Mount et al. (1997) reported the 24, 48, and 96 h LC_{50} of *P. promelas* and $CaSO_4$ to each be >1.97 g/L.

Survival of both *C. dilutus* and *H. azteca* were unaffected by dilutions of FGD gypsum:control sediment up to 50:50 (Table 2). The only significant impairment noted in these exposures was a decrease in *C. dilutus* growth at the FGD gypsum: control sediment dilution of 25:75. However, survival of *C. dilutus* at this mixture was 100%. To our knowledge this is the first study reporting FGD gypsum ($CaSO_4$) effects on sediment-dwelling organisms.

Ecotoxicity assessments are important due to FGD gypsum's increased and effective use in agricultural settings, as well as its environmental persistence. According to Feldhake et al. (2001), 46% of applied gypsum calcium was still present in the top 40 cm of soil, following two growing seasons and 1.7 m of total rainfall. Favaretto et al. (2006) reported mass loss in runoff decreases of 85%, 60%, 80%, and 59% for dissolved reactive phosphorus, total phosphorus, soluble ammonium, and total nitrogen, respectively, where gypsum had been applied. Reduction of runoff by 67% in gypsum-treated areas, as opposed to control areas, was reported by Zhang et al. (1998). This same study noted that 5 months after gypsum surface application, runoff was still being significantly reduced. Gypsum has also shown success in nutrient reduction when applied to grass buffer strips. Soluble P concentrations were reduced 32–40% in surface runoff of strips treated with gypsum versus only 18% reduction in strips left untreated (Watts and Torbert 2009). Feldhake et al. (2001) reported maximum gypsum concentrations in stream flow during storm events of 34 mg/L. Based on current acute and chronic toxicity assessments, recommended agricultural gypsum applications pose no observed threat to aquatic macroinvertebrates.

Acknowledgments Mention of trade names or commercial products are solely for the purpose of providing specific information and do not imply recommendation or endorsement by the US Department of Agriculture.

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