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Suppression of rice methane emission by sulfate deposition in simulated acid rain

Vincent Gauci,[1] Nancy B. Dise,[2] Graham Howell,[1] and Meaghan E. Jenkins[1,3]

[1]   Sulfate in acid rain is known to suppress methane (CH_4) emissions from natural freshwater wetlands. Here we examine the possibility that CH_4 emissions from rice agriculture may be similarly affected by acid rain, a major and increasing pollution problem in Asia. Our findings suggest that acid rain rates of SO_4^{2-} deposition may help to reduce CH_4 emissions from rice agriculture. Emissions from rice plants treated with simulated acid rain at levels of SO_4^{2-} consistent with the range of deposition in Asia were reduced by 24% during the grain filling and ripening stage of the rice season which accounts for 50% of the overall CH_4 that is normally emitted in a rice season. A single application of SO_4^{2-} at a comparable level reduced CH_4 emission by 43%. We hypothesize that the reduction in CH_4 emission may be due to a combination of effects. The first mechanism is that the low rates of SO_4^{2-} may be sufficient to boost yields of rice and, in so doing, may cause a reduction in root exudates to the rhizosphere, a key substrate source for methanogenesis. Decreasing a major substrate source for methanogens is also likely to intensify competition with sulfate-reducing microorganisms for whom prior SO_4^{2-} limitation had been lifted by the simulated acid rain S deposition.

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1. Introduction

[2]   Methane (CH_4) is a potent greenhouse gas which is estimated to have contributed ∼50% of the enhanced climate forcing of CO_2 since 1850 [*Hansen et al.*, 2000]. Many of the sources of CH_4, both natural and anthropogenic, are reasonably well constrained within global budgets, the principal exception being rice agriculture emissions where estimates range from 20 to 100 Tg of the estimated total source of ∼540 Tg [*IPCC*, 1996]. Despite tremendous growth in rice production due to 'green revolution' methods employed since the 1960s, recent estimates point to a rice CH_4 source at the lower end of this range [*Denier van der Gon*, 2000] with a projected likely declining trend in emissions as harvest area decreases and agricultural practices with respect to water management and fertilizer use change [*Khalil and Shearer*, 2006]. In rice agro-ecosystems such management practices are a key determinant of the output of CH_4. Methanogenesis is a strictly anaerobic process and so the duration of paddy inundation and the employment of mid-season field drainage both contribute to defining the maximum potential CH_4 that is produced versus that which is oxidised in the rhizosphere. This interplay between CH_4 production and oxidation may be further altered by the application of ammonium fertilizers [*Bodelier et al.*, 2000] which may enhance the methanotrophic potential of paddy soil through reducing nitrogen limitation in methanotrophs [*Bodelier et al.*, 2000].

[3]   As well as nitrogen additions in the form of fertilizer, large individual applications of SO_4^{2-} (10^2-10^3 kg SO_4^{2-}-S ha^{-1}) are increasingly being applied to rice paddies in order to meet the biological sulfate demand of rice plants. Such additions are known to suppress methane emissions from rice paddies by up to ∼70% [*Denier van der Gon et al.*, 2001, and references therein]. The application of large quantities of SO_4^{2-} amendments to rice paddies has therefore been proposed as a greenhouse gas mitigation strategy [*Denier van der Gon et al.*, 2001]. In natural peatlands, research has established that very low rates of SO_4^{2-} deposition (∼25 kg SO_4^{2-}-S ha^{-1} yr^{-1} as small weekly pulses), similar to those of regions experiencing acid rain pollution, suppress methane emissions by as much as 30–40% [*Dise and Verry*, 2001; *Gauci et al.*, 2002]. As with the effect of sulfate amendments on rice CH_4 emissions, it is thought that this is due to stimulation of sulfate-reducing microbial populations that out-compete methane producers for substrates [*Gauci and Chapman*, 2006]. For natural wetlands, this interaction may be important in offsetting the climate change-related growth in CH_4 emission from these ecosystems up until the middle of the 21st century [*Gauci et al.*, 2004a].

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[4] The effect of acid rain rates of SO_4^{2-} introduced to wetlands may be long-lasting, with treatment effects continuing to suppress methane emissions (by 30–40%) more than 2 years after the end of an acid rain simulation [*Gauci et al.*, 2005]. This indicates that the available SO_4^{2-} pool is continually being replenished through recycling at the steep redox gradients that exist primarily in the rhizosphere of these systems, such that more moles of CH$_4$ are suppressed by a mole of SO_4^{2-} than the 1:1 reaction stoichiometry would suggest. Indeed up to 8.5 moles of CH$_4$ were suppressed per mole of applied acid rain simulant in this long-term Scottish peatland experiment [*Gauci et al.*, 2005].

[5] Such recycling is also thought to occur in rice paddy soils where SO_4^{2-} applications suppressed CH$_4$ emissions to a greater extent than the stoichiometric potential of the applied sulfate containing amendment would suggest [*Denier van der Gon et al.*, 2001]. Given that rice CH$_4$ emissions seem to respond similarly to applied sulfate in terms of CH$_4$ emissions as do natural wetlands, the possibility arises that sulfate inadvertently applied through industrial pollutant emissions, atmospheric chemical transformation and subsequent deposition may similarly impact rice CH$_4$ emissions.

[6] Asia, as a consequence of rapid economic growth and limited pollution controls, has been a major and growing source of SO$_2$ to the atmosphere such that the region is currently contributing ∼46% of the global SO$_2$ source [*Smith et al.*, 2001]. This is in contrast with higher latitude industrialised nations where SO$_2$ emissions have declined substantially since the 1970s. This global shift in anthropogenic sulfur emissions and deposition [*Duan et al.*, 2007] means that Asian wetlands and rice agro-ecosystems will become the most impacted by S in the world and that this new source of S may significantly reduce CH$_4$ emissions from these ecosystems. Rice agriculture may be particularly affected since rice paddies are often not far removed from major industrial areas. Given that Asia produces the majority of the world's rice and is experiencing this dramatic increase in acid rain pollution [*Rodhe*, 1999] we examine the potential effect of acid rain rates of SO_4^{2-} deposition on CH$_4$ emission from rice agro-ecosystems.

[7] In this paper we detail the effect of an acid rain simulation experiment on rice mesocosm CH$_4$ emissions. In doing so we compare the effect of two modes and levels of sulfate application that are representative of sulfate applied either indirectly, through acid rain, or directly through the application of individual pulses of applied sulfate albeit within an annual acid rain S deposition range.

2. Methods

2.1. Rice Soils Collection and Mesocosm Preparation

[8] After considering SO_4^{2-} deposition data we collected paddy soil prior to planting from Monte dos Alhos in Portugal (37:53°N, 8:27°W) in early 2004. In terms of S deposition, this area is relatively unpolluted (S deposition ∼5 kg ha^{-1}yr^{-1}) since most deposition is from relatively clean air masses derived from the Atlantic Ocean.

[9] In order to approximate the SO_4^{2-} concentration measured in the field, the following soil mix was prepared from the Portuguese soil: 50% coarse sand (horticultural grade, acid washed, leached with dH$_2$O to remove residual

SO_4^{2-}), 30% fine sand (horticultural grade sharp sand), 10% rice-paddy soil from Portugal, 5% peat and 5% part fine-ground silica. This diluted paddy soil ensured the presence of the same microbial communities that exist in rice soil and approximated the texture of the parent soil.

2.2. Rice Growing and Treatments

[10] Rice seeds from the Zeus japonica cultivar (*Oryza sativa* L) were used for this experiment. This variety was chosen as it is commonly grown in the region from which the soil was collected. The rice seeds were first germinated in the dark on John Innes seed compost and then grown in trays until they reached a height of approximately 10 cm. The seedlings were then planted directly into rice soil mesocosms (4 plants per mesocosm 30 cm diameter × 40 cm depth). The twelve mesocosms were fertilized with a balanced fertiliser (Miracle-Gro) at 8.48g/mesocosm (applied diluted in dH$_2$O). This is equivalent to 1200 kg ha^{-1} of fertilizer and approximated N, P, K inputs annually applied to the original farm paddy soil. Rice plants were then grown under artificial lighting conditions (∼300 μE m^{-2}, 12 h day^{-1}) that remained constant during the monitoring period i.e., early September to late November 2004. The mesocosms were randomly allocated to the following treatments (with 4 replicates per treatment): (1) regular small weekly applications of Na$_2$SO$_4$ at an annualised rate of 100 kg SO_4^{2-} -S ha^{-1} yr^{-1}, a rate of acid rain S deposition commonly experienced in NE China; (2) a single application of 100 kg SO_4^{2-} -S ha^{-1} to replicate modes of sulfate application currently proposed as CH$_4$ mitigations strategies [*Denier van der Gon et al.*, 2001]; and one set of controls where only deionised water and fertilizer were added. The small regular additions applied at a rate of 100 kg SO_4^{2-} -S ha^{-1} yr^{-1} amounted to a total SO_4^{2-} deposition of ∼20 kg SO_4^{2-} -S ha^{-1} throughout the duration of the study. A rhizon™ porous ceramic pore water sampler was positioned horizontally at 10 cm beneath the soil surface (Figure 1). This facilitated repeated (weekly) sampling of rhizosphere pore water for analysis of SO_4^{2-} (via ion chromatography, Dionex) and for dissolved CH$_4$ [*Gauci et al.*, 2004b].

2.3. CH$_4$ Flux Measurements

[11] Methane emissions were measured from each monolith once a week via a static chamber technique. In the middle part of each sampling day samples were taken from a headspace volume that was defined by temporarily sealing a chamber onto the monolith for 40 min (Figure 1). The chamber contained a fan which allowed good mixing of headspace gases during incubation. During the period of incubation, a 60 ml air sample was withdrawn from each chamber at 0, 20 and 40 min. Samples were analyzed for CH$_4$ content by GC FID and CH$_4$ fluxes were calculated. A chamber extension collar was used to minimize damage to plants once they had reached the maximum height of the chamber.

[12] Ancillary measurements made included soil and air temperature; plant height; tiller number; root, shoot, and grain dry-weight; total C, N, S of root, shoot, and grain and plant morphological observations (e.g., timing of spikelet formation, filling of panicles etc). Results were analyzed for
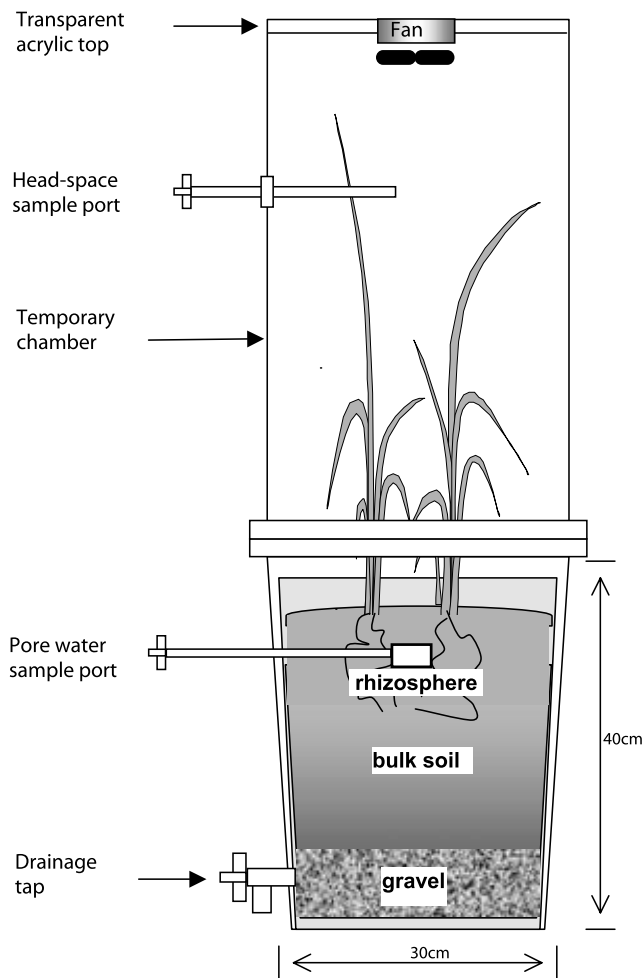
Figure 1. Schematic of experimental gas exchange chamber design.

statistical differences using repeated measures analysis of variance (General MANOVA; Minitab release 14).

3. Results and Discussion

[13] Over the duration of the experiment, CH$_4$ emission was lower from both sulfate treatments relative to controls. This decrease was significant for the single application of 100 kg S ha^{-1} treatment, where CH$_4$ emission was reduced by up to one third (p < 0.01; Table 1). Methane emissions from control mesocosms followed a pattern of almost linear increase beyond day 14, progressively increasing in CH$_4$ output until reaching a peak in emission in day 56 of 174 mg CH$_4$ m^{-2} day^{-1} (Figure 2). In contrast, both of the sulfate treatments demonstrated reductions in CH$_4$ emission growth between days 28 and 38, and lower CH$_4$ emissions during the peak emission period exhibited by the controls (121 mg CH$_4$ m^{-2} day^{-1} in the acid rain simulation and 99 mg CH$_4$ m^{-2} day^{-1} in the single sulfate pulse mesocosms) (Figure 2). Broad patterns in CH$_4$ emission growth reflect changes in pore water dissolved CH$_4$ and SO$_4^{2-}$ concentration (Figure 3). For the large single SO$_4^{2-}$ application treatment the onset of growth in CH$_4$ production is delayed relative to controls and the acid rain simulation treatment until after day 35 (Figure 3b). Dissolved CH$_4$ concentrations peaked at ~120 μmol L^{-1} for both controls and acid rain simulation treatment on day 70 but only peaked at ~80 μmol L^{-1} in the large single SO$_4^{2-}$ application. Dissolved CH$_4$ concentrations were significantly lower in the large single SO$_4^{2-}$ application than in either the controls or the acid rain simulation (p < 0.001, General MANOVA) (Figure 3b).

[14] Dissolved SO$_4^{2-}$ concentrations were an order of magnitude higher in the single SO$_4^{2-}$ application mesocosms than in the control and acid rain simulation mesocosms during the first 30 d. Concentrations peaked on day 14, reflecting the period required for the dissolved SO$_4^{2-}$ to percolate down to the rhizon pore water collection point 10 cm below the soil sediment/paddy water interface (Figure 3a). As with dissolved CH$_4$ concentrations there was no difference between control and acid rain SO$_4^{2-}$ simulation treatments throughout the duration of the monitoring period. This may not reflect differences in in situ sulfate reduction rates since increased sulfate-reducing activity may accelerate S cycling such that instantaneous SO$_4^{2-}$ concentrations are unaffected or may even be reduced [*Gauci et al.*, 2002; *Gauci and Chapman*, 2006]. Given that pore water concentrations were measured at only one depth, the possibility remains that any differences in CH$_4$ concentration between the acid rain simulation treatments and controls were located elsewhere in the mesocosm soil profile.

Table 1. Summary Table of CH$_4$ Emission Response to Experimental SO$_4^{2-}$ Addition[a]

Treatment	Mean CH$_4$ Flux ($\pm$SE) (mg CH$_4$ m^{-2} d^{-1})	Total CH$_4$ Emission (g CH$_4$ m^{-2})	Percent Suppression (Treatment Versus Control)	P–Value (MANOVA)
Duration of Experiment (Day 1–77) n = 60				
Control	82.9 (8.8)	6.61		
100 kg S ha^{-1}y^1	75.3 (6.8)	5.74	13	n.s.
100 kg S ha^{-1}	64.0 (8.8)	4.86	31	<0.01
Grain Filling/Ripening Stage (Day 38–63) n = 20				
Control	134 (14.8)	3.65		
100 kg S ha^{-1}y^1	103 (8.8)	2.77	24	<0.05
100 kg S ha^{-1}	86 (10.5)	2.45	43	<0.05

[a]Here P values denote the significance level of any difference between individual treatments and the control.
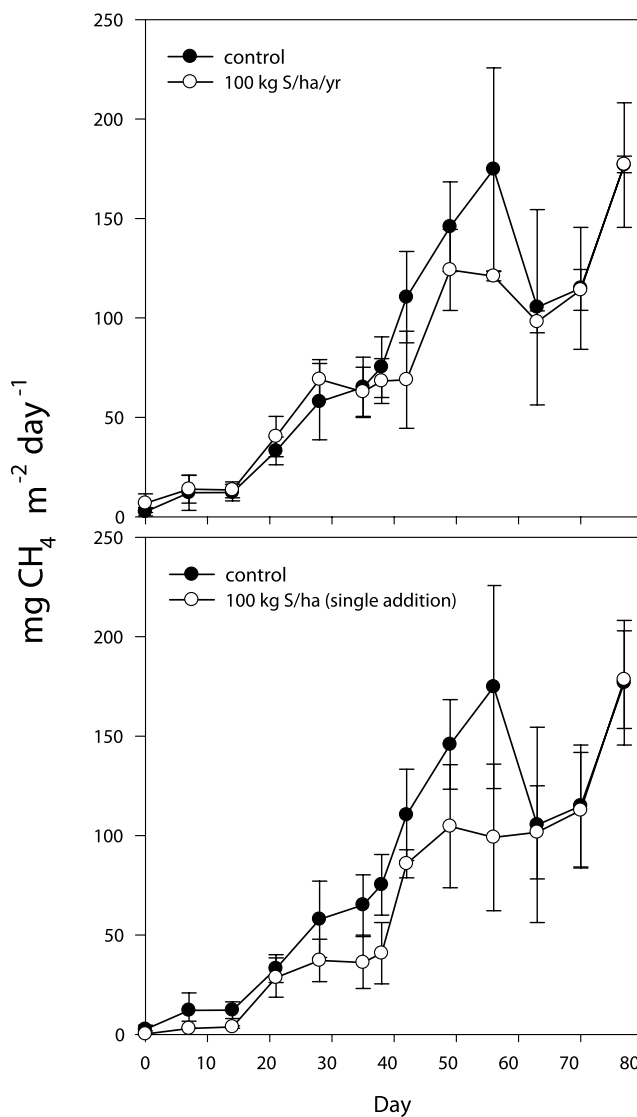
Figure 2. Methane emission from SO_4^{2-} treated and control rice mesocosms. Each point represents the mean CH_4 flux from four mesocosms. Error bars represent ±1 SE of the mean.

[15] The observed period of reduced CH_4 emission growth rate in SO_4^{2-} treated mesocosms coincides with the first appearance of panicles on the rice plants (day 28) and continued until all panicles had formed and flowered (by day 38). During the ensuing grain-filling stage, the cumulative small applications of sulfate in the acid rain simulation were sufficient to suppress emissions by 24% ($p < 0.05$; Table 1), an important reduction in CH_4 emission given that this period constituted ∼50% of the total CH_4 that was emitted during the experiment. During this period, CH_4 emission from the single 100 kg S ha^{-1} treatment was significantly suppressed by 43% relative to controls ($p < 0.05$; Table 1). Suppressed emitted CH_4:SO_4^{2-} ratios were, over the entire experiment, 26 and 11 for the continuous and single sulfate application modes respectively, and 32 and 7.5 for the same treatments during grain filling and ripening. For the small continuous SO_4^{2-} applications these are the highest ratios recorded for terrestrial soil CH_4 emission

studies, implying extensive recycling of S in the rhizosphere should all CH_4 suppression be attributable to this single mechanism.

[16] The timing of the maximum period of suppression (grain filling and ripening) suggests that substrate supply via rhizodeposition of photosynthetically fixed carbon may be a major control in determining the extent of competition between sulfate-reducing bacteria and methanogens. Given that the hypothesized interaction between sulfate-reducing bacteria and methanogens is dependent on a limiting supply of substrate over which competitive exclusion of methanogens may occur, this period of maximum suppression may be taking place during a period of reduced rhizodeposition. Grain filling and ripening requires a substantial proportion
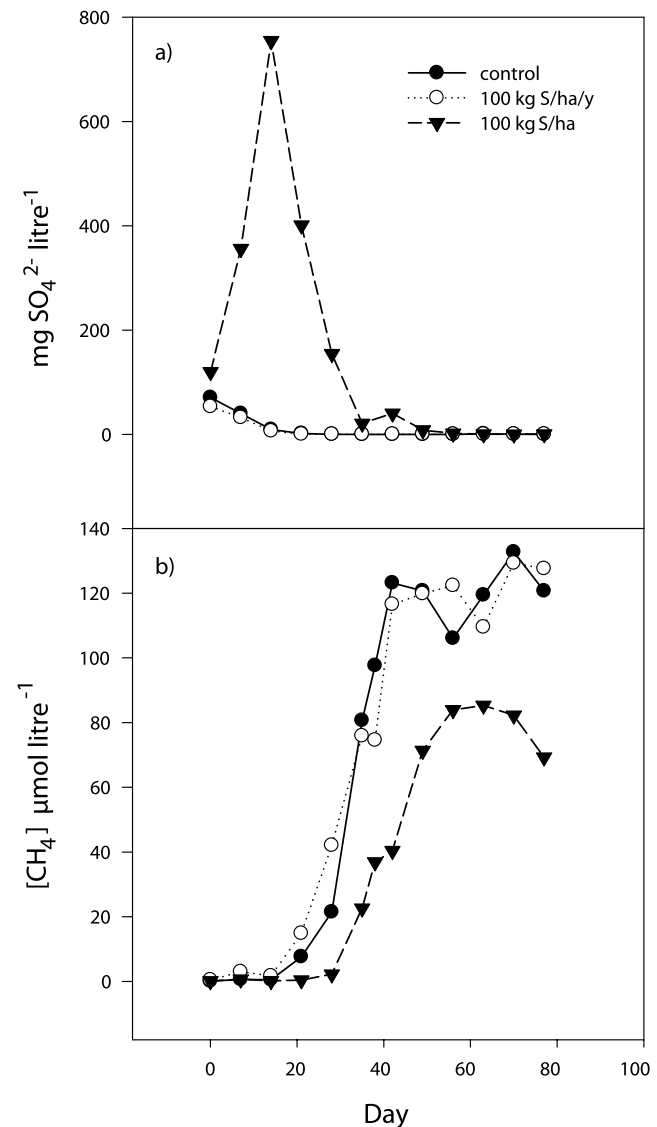

Figure 3. (a) Dissolved SO_4^{2-} concentrations in pore water from the two modes of SO_4^{2-} treatment and controls. Points represent the mean of four measurements. Error bars are omitted for clarity. (b) Dissolved CH_4 concentration in mesocosm pore water (sampled at 10 cm beneath the soil surface/paddy water interface) for the two modes of SO_4^{2-} treatment and controls.
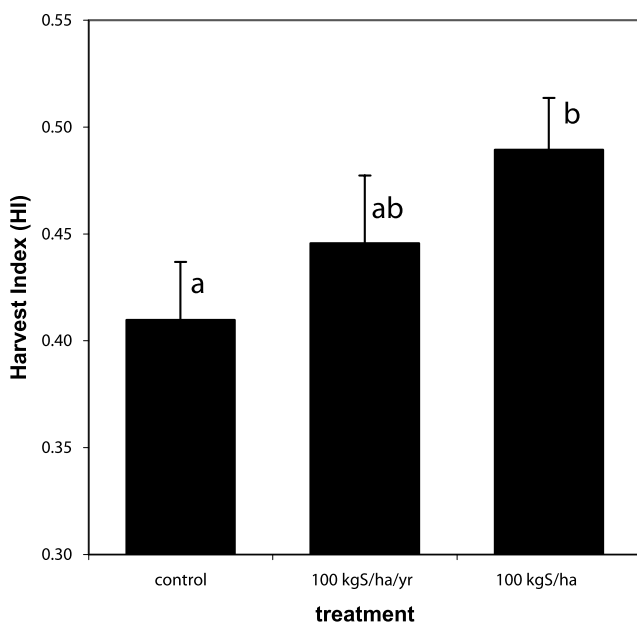
Figure 4. Changes in rice harvest index (HI) with applied SO_4^{2-}. Error bars represent +1 SE of the mean. Bars with the same letter do not differ at the $p < 0.05$ level, ANOVA.

of the total carbon that is photosynthetically fixed by the plant [*Denier van der Gon et al.*, 2002] some of which would otherwise be rhizodeposited and so there is likely to be an important link between the proportion of photosynthate that is directed to grain production, and the susceptibility of CH₄ emissions to SO_4^{2-} deposition via acid rain.

[17] *Denier van der Gon et al.* [2002] identify an inverse relationship between grain yield and CH₄ emission that is determined by the relative proportion of photosynthate being directed to either grain production or rhizospheric C leakage via exudation. Given that SO_4- is increasingly applied to rice systems to assist with grain production (by alleviating soil S depletion), there is at least the possibility of an alternative mechanism that may contribute to the effect of SO_4^{2-} on CH₄ emissions, be it applied intentionally through soil amendments or unintentionally via acid deposition i.e., a yield-enhanced reduction in methanogenic substrate. We identify a trend of increasing harvest index (HI, calculated as dry weight of harvested grain divided by above ground biomass) in response to increased SO_4^{2-} supply via the two modes of application (Figure 4), the difference being significant between the large single application and the controls ($p < 0.05$, ANOVA). This finding supports the likelihood that any S-induced increases in yield limit methanogenesis via a combination of two mechanisms: (1) reducing substrate supply to the rhizosphere and methanogens within it (through redirection of photosynthate to grain production) and (2) promoting competitive interactions between sulfate reducers and methanogens over increasingly limited substrate supplies.

4. Summary and Implications

[18] Our experimental findings demonstrate that SO_4^{2-} applied at rates within the range experienced in acid rain-

impacted regions such as Asia is capable of substantially suppressing CH₄ emissions. Significant CH₄ suppression was measured during the rice grain filling and ripening stage of plant development, which constitutes ~50% of the total CH₄ that is emitted by controls (Table 1). This temporal feature, together with a trend of increasing harvest index with increasing applied total SO_4^{2-}, suggests that SO_4^{2-} influences over rhizodeposited exudate supply may exert an overall control on methanogens via 2 mechanisms: (1) the limitation of substrate supply while (2) simultaneously providing a more competitive environment in which competition with sulfate reducers intensifies.

[19] Estimated mean total annual SO_4^{2-} -S deposition in the region ranges from ~30 kg SO_4^{2-} -S ha^{-1} yr^{-1} in S. East Asia to ~85 kg SO_4^{2-} -S ha^{-1} yr^{-1} in East Asia [*Dentener et al.*, 2006] although areas within East Asia (e.g., the North) may receive considerably more S deposition. These values are similar to the total SO_4^{2-} applied in both the small continuous acid rain simulation (~20 kg SO_4^{2-} -S ha^{-1}) and in the single application of 100 kg SO_4^{2-} -S ha^{-1}. Our experimental approach denied SO_4^{2-} treated mesocosms a history of aerially deposited SO_4^{2-} and so represents the situation at the outset of a pollution episode. Given that periods of drought in natural wetlands (an analogous situation to regular dry periods between periods of inundation in rice agriculture) are known to replenish the supply of SO_4^{2-} from reduced S forms [*Dowrick et al.*, 2006], the CH₄ response to acid rain S deposition may, in nature, respond to cumulative S deposition over many years even if a component of the deposited SO_4^{2-} was to be dispersed in drainage waters. Our findings may therefore underestimate the overall CH₄ suppression response to prolonged periods of acid deposition and SO_4^{2-} replenishment through periodic paddy drainage.

[20] By 2030 pollutant S deposition is predicted to significantly worsen with deposition under the most pessimistic IPCC Special Report on Emissions Scenarios (SRES) scenario ranging from ~88 kg SO_4^{2-} -S ha^{-1} yr^{-1} in S. East Asia to ~130 kg SO_4^{2-} -S ha^{-1} yr^{-1} in East Asia and, highest, ~150 kg SO_4^{2-} -S ha^{-1} yr^{-1} in South Asia [*Dentener et al.*, 2006], well within the range of S application shown to reduce CH₄ emissions [*Denier van der Gon et al.*, 2001] and therefore negating the need for costly SO_4^{2-} amendments to meet the biological demands of rice plant growth. A repeat of this study for a range of commonly grown rice cultivars and commonly farmed soil types under different management regimes would ensure that the full response range of rice CH₄ emission to acid rain is properly characterized for Asia.

[21] In conclusion, our results point to a hitherto overlooked factor that, in addition to recognized changes in management practices [*Khalil and Shearer*, 2006], may be progressively reducing CH₄ emissions from rice agriculture. Our findings suggest that acid rain rates of SO_4^{2-} deposition may help to reduce CH₄ emissions from rice through a combination of mechanisms. The first mechanism is that the low rates of SO_4^{2-} supply may be sufficient to boost yields of rice and, in so doing, causes a reduction in root exudates to the rhizosphere, a key substrate source for methanogenesis. The role of substrate limitation is further supported by the observation that SO_4^{2-} suppression of CH₄ emission was greatest during the energy demanding grain production

and ripening stage. This suggests that photosynthate leakage to the rhizosphere was reduced owing to the greater energy demands required by reproduction. Decreasing a major substrate source for methanogens is likely to fuel competition with sulfate reducing microorganisms for whom SO_4^{2-} availability had been limiting prior to the onset of simulated acid rain S deposition.

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