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Authors

Redeker, KR
Meinardi, S
Blake, D
et al.

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Gaseous emissions from flooded rice paddy agriculture

K. R. Redeker,[1] S. Meinardi, and D. Blake

Department of Earth System Science, University of California, Irvine, California, USA

R. Sass

Department of Ecology and Evolutionary Biology, Rice University, Houston, Texas, USA

[1]   Modification of continental land for agricultural use has increased over the last century. Atmospheric impact of this land use change has only been addressed for a few ecosystems and compounds. This paper provides, to date, the most comprehensive examination of gaseous emissions from rice paddies. We report seasonal emission ranges and integrated emission totals for 55 chemical species. This paper is the first to report emissions of isoprene, ethyl chloride, bromoform, alkyl nitrates, bromodichloromethane, hexane, and benzene from rice paddies. Emissions of alkyl nitrates, bromoform, ethyl chloride, and bromodichloromethane by terrestrial ecosystems have never before been observed. For species where emissions were observed we tentatively ascribe possible mechanisms of production; photochemical or biological production in the water column or rice plant mediated. For some compounds, during periods of maximum emissions, ambient rice paddy air concentrations may be concentrated enough to affect regional atmospheric chemistry.   *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 1610 Global Change: Atmosphere (0315, 0325); *KEYWORDS:* rice paddies, gaseous emissions, hydrocarbons, halocarbons, alkyl nitrates

1.   Introduction

[2]   Six crops (barley, maize, oats, potatoes, rice, and wheat) cover 4.5% of the global continental surface area (Statistics Norway, available at http://www.ssb.no/english/yearbook/tab/t-intnasj-663.html, 2001). Various ecosystems have been displaced through human agriculture, with the majority of media and research attention focusing on the recent slash-and-burn transformation of Amazonian rain forest into temporary use agricultural land. An understanding of the emissions of crops and the ecosystems that have been, and are currently being, replaced is necessary to fully describe the impact of agriculture on atmospheric chemistry.

[3]   In 1951, flooded rice paddies covered 0.75% of the continental surface area (1.04×10^{12} m^2), which increased to 1.1% of the continental surface area by 1990 [*International Rice Research Institute* (*IRRI*), 1995]. Because of population increases and the subsequent demand for food, rice paddies have been estimated to increase from the current 1.2% coverage to over 1.6% of the entire continental surface area by 2025 [*Anastasi et al.*, 1992] (Statistics Norway, available at http://www.ssb.no/english/yearbook/tab/t-intnasj-663.html, 2001).

[4]   Several globally significant atmospheric molecules have been linked to rice paddy agriculture. Greenhouse gases (methane and nitrous oxide), ozone depleting compounds (halocarbons, including methyl halides), smog precursors (volatile organic compounds and nitrogen-bearing compounds), and aerosol precursors (dimethyl sulfide and methyl iodide) are all released from rice paddies [*Cicerone and Oremland*, 1988; *Kanda et al.*, 1992; *Khalil et al.*, 1990, 1998; *Neue and Sass*, 1994; *O'Dowd et al.*, 2002; *Redeker et al.*, 2000, 2002; *Yang et al.*, 1998]. Elevated soil temperatures and atmospheric carbon dioxide concentrations cause increased emissions of methane from rice paddies [*Ziska et al.*, 1998] while higher atmospheric temperatures increase methyl bromide and methyl iodide fluxes (K. R. Redeker and R. J. Cicerone, Environmental controls over methyl halides emissions from rice paddies, submitted to *Global Biogeochemical Cycles*, 2003, hereinafter referred to as Redeker and Cicerone, submitted manuscript, 2003). This raises the question of how other rice paddy emissions may be affected by concurrent changes in climate and paddy coverage. A baseline of emissions from rice paddies will be necessary to determine regional and global impacts of rice agriculture and will allow quantification of the effects of climate change on these emissions.

[5]   Previous surveys have been published, including those by *Lamb et al.* [1987], *Winer et al.* [1992], *Kanda et al.* [1992], *Minami* [1994], and *Khalil et al.* [1998], for

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[1]Now at QUESTOR Centre, Queen's University of Belfast, Belfast, UK.

rice paddies and maize and wheat agriculture. These studies cover certain suites of compounds (notably ≤C4 hydrocarbons and sulfur-bearing gases) but are not fully representative of field emissions. Several of these studies relied on limited temporal (one or two sampling dates during the season) and/or spatial (two chamber replicates) sampling schemes, which produce less accurate field estimates for methyl halides [*Redeker et al.*, 2002] but appear to generate acceptable values for methane [*Sass et al.*, 2002]. This study is, to date, the most representative and comprehensive survey of rice paddy agricultural emissions including alkanes, alkenes, aromatics, halocarbons, and sulfur- and nitrogen-bearing compounds. CFC and halon concentrations were also studied, primarily as a methodological control (most CFCs and halons should be unaffected by interaction with the ecosystem or the sampling and analysis process and thus should have no discernible emissions).

[6] In Houston, Texas during the 2000 growing season we surveyed emissions from a commercial rice paddy from the late tillering (vegetative) stage through the early ripening phase of rice growth. Our full season results describing methane and methyl halide fluxes and field variability are described in other papers [*Sass et al.*, 2002; *Redeker et al.*, 2002] and will be mentioned only briefly here. In this paper we report the emissions (or lack thereof) of 54 separate compounds from rice paddies (Table 1). Emissions are tentatively classified as driven by paddy water photochemistry, biology in the paddy water column, or as mediated by the rice plant (including both transport through the rice plant from the soil to the atmosphere and gases produced and transported by the plant itself). Emissions from residue burning (based on agricultural estimates from *Andreae and Merlet* [2001]) are also included for comparison to seasonal rice paddy emissions and to provide a more complete description of annual rice paddy atmospheric impact.

[7] This study does not report any diurnal data. For this reason along with many other parameters that may change from field to field this study does not attempt to define global emissions of these compounds from rice paddies. Any calculated global emissions are provided only as a means to estimate the potential level of importance rice paddies might have for any given compound. The effect of several parameters on emissions of methyl halides from rice paddies is described by Redeker and Cicerone (submitted manuscript, 2003). A description of the effects of these and other parameters on methane production in rice paddies can be found in the work of *Bossio et al.* [1999], *van der Gon* [1999], *Neue and Sass* [1994], and *Wang et al.* [1997].

2. Methods

2.1. Rice Growth Stages and Field Parameters

[8] To be accurate, rice paddy emissions must be characterized during the vegetative, reproductive, and ripening stages [*Redeker et al.*, 2000]. The vegetative stage (from planting to about day 70) occurs as the plant expends its energy on rapid growth. During this phase the number of tillers (or shoots) and the plant height expand very quickly. Up to 2 cm of plant height increase may be observed on a

daily basis. Maximum tillering, which, at Houston, occurred near day 60, is described as the point at which the gradient of tiller number with time is at a maximum. We define it for this study as the date at which the rice achieved maximum growth.

[9] After the vegetative stage, rice begins the reproductive stage (from about day 70 to harvest). This is marked by the initiation of the panicle, the stem on which the grain forms and matures. In Houston, maximum tillering and panicle initiation occurred at nearly the same time. The panicle grows through the rice stalk and exits (Heading), after which the plant develops flowers (Flowering or Anthesis). In Houston these steps occurred near days 85 and 100. After flowering, the plant devotes its resources toward grain development and the rest of the season follows the ripening stage until harvest, which occurred in Houston on day 140. A more detailed description of rice growth stages can be found in the work of the *Rice Information Cooperative Effort* (*RICE*) [1967].

[10] The fields in Houston were drill-planted in rows with a 7.6-cm separation between plants. The cultivar grown was Cocodrie, a newer Texan variety that was bred from L202/Cypress/Tebonnet varieties. The fields were flooded to provide soil moisture just after planting and then were allowed to drain and remain dry until day 45, when they were flooded again. After day 45, the fields remained flooded until just prior to harvest (about day 130 after planting) when field drainage was begun to allow the harvesting combines access to the field. The drainage period lasts for several days, and the last sampling date, 131 days after planting, occurred during this process. The soil in the paddy field was dry and solid before day 45 and after day 138–140. During periods of flooding, direct access from the soil to the atmosphere is very limited, with ebullition providing a minor pathway for communication. The rice plant provides the main conduit for soil-atmosphere communication, complicating assessment of whether compounds are produced by the rice plant or merely transported by it.

[11] The conditions of the paddies in Houston are different in many ways from conditions around the world. A comparison of field conditions between Houston, Texas and Maxwell, California can be found in the work of *Redeker et al.* [2002]. Major possible differences between the fields described in this study and other fields found globally are (1) flooding conditions, (2) soil parameters including diffusivity, along with soil carbon and halide concentrations, (3) fertilizer used and frequency of application, (4) rice cultivar, (5) whether the rice is transplanted, broadcast by plane over the field, or drill-planted, and (6) soil, water, and air temperature of the field. To date, most field residues are burned to reinvigorate the soil and diminish the risk of various crop diseases.

2.2. Chamber-Sampling Methodology

[12] The following descriptions are pertinent to all measured gases except methane; measurement techniques and methodologies for methane data can be found in the work of *Sass et al.* [2002]. The field design in Houston is shown in Figure 1. Three boardwalks were placed in the field, each 22 m in length. At the end of each boardwalk a chamber base was inserted before the fields were flooded. A breakdown in the planting machinery created a convenient swath that we

Table 1. Observed and Estimated Emissions From Rice Paddies[a]

	Instantaneous Emissions		Integrated Seasonal Emissions				
Compound	Range of Emissions, $\mu g\ m^{-2}\ hr^{-1}$	Median Emission, $\mu g\ m^{-2}\ hr^{-1}$	Planted Chambers, $mg\ m^{-2}$	Control Chambers, $mg\ m^{-2}$	Accuracy of reported value, ±%	Biomass Burning, $mg\ m^{-2b,c}$	Likely Region of Origin for Compound
Hydrocarbons							
			Alkanes				
methane	**27 to 13000**	**7300**	**12000 ± 1700**		1[d]	**2000**	**rice**
ethane	0.59 to 2.7	0.87	1.8 ± 1.4	1.8	10[d]	730	
propane	−0.06 to 1.3	0.59	0.88 ± 0.58	0.94	10[d]	390	
i-butane	−0.63 to 0.64	0.29	0.31 ± 0.39	0.15	10[d]	11	
n-butane	−3.7 to 0.70	0.25	0.48 ± 0.35	0.71	10[d]	45	
i-pentane	−1.2 to 0.76	0.15	0.11 ± 0.40	−0.41	10[d]	6	
n-pentane	−5.6 to 20.	−0.38	1.6 ± 3.8	−5.5	10[d]	19	
cyclopentane	<0.33	<0.33	<0.79		10[d]	NR	
hexane	**−0.02 to 0.48**	**0.20**	**0.23 ± 0.12**	**0.14**	10[e]	**38**	**paddy/rice**
methylcyclopentane	<0.20	<0.20	<0.47		10[d]	NR	
cyclohexane	<0.23	<0.23	<0.51		10[d]	NR	
heptane	<0.23	<0.23	<0.56		10[d]	60	
methylcyclohexane	<0.27	<0.27	<0.64		10[d]	NR	
trimethylpentane	<0.27	<0.27	<0.64		10[e]	NR	
			Alkenes and Alkynes				
ethene	**3.1 to 6.2**	**3.8**	**5.8 ± 1.3**	**5.2**	10[d]	**1100**	**photochem**
ethyne	−0.010 to 0.075	0.039	0.06 ± 0.07	0.08	10[d]	270	
propene	**1.5 to 2.8**	**1.9**	**2.5 ± 0.6**	**2.5**	10[d]	**750**	**photochem**
1-butene	**0.47 to 2.3**	**1.7**	**1.7 ± 0.4**	**1.4**	10[d]	**98**	**photo/rice**
t-2-butene	**0.47 to 1**	**0.70**	**0.70 ± 0.52**	**0.55**	10[d]	**30**	**photochem**
c-2-butene	**<0.15 to 0.21**	**see text**	**0.04 ± 0.04**	**0.05**	10[d]	**38**	**photochem**
1,3-butadiene	<0.25	<0.25	<0.61		10[d]	68	
2-methyl-1-butene	<0.33	<0.33	<0.79		10[d]	5	
3-methyl-1-butene	<0.33	<0.33	<0.79		10[d]	5	
isoprene	**3.5 to 11**	**4.3**	**8.9 ± 2.7**	**1.7**	10[f]	**38**	**rice**
			Aromatics				
benzene	**−0.12 to 1.1**	**0.33**	**0.60 ± 0.56**	**0.69**	10[d]	**110**	**paddy**
toluene	0.01 to 6.6	1.7	3.1 ± 4.8	6	10[d]	20	
o-xylene	−0.00 to 1.7	0.30	0.5 ± 1.4	1	11[e]	3	
p-xylene	−0.11 to 2.5	0.14	0.6 ± 1.2	0.8	11[e]	3	
m-xylene	−0.49 to 2.6	0.42	0.7 ± 1.8	1.5	11[e]	3	
ethylbenzene	−0.17 to 0.78	−0.01	0.19 ± 0.70	0.57	11[e]	23	
			Other Compounds				
Monoterpenes			**0.35**[f]			**11**	**rice**
Halocarbons, CFCs							
			CFCs and Halons				
CFC11	0.01 to 0.21	0.10	0.15 ± 0.16	0.04	2.2[g]	NR	
CFC12	0.06 to 0.30	0.10	0.15 ± 0.32	0.08	2.2[g]	NR	
CFC113	−0.58 to 3.5	1.2	2 ± 2.9	3.5	2.8[g]	NR	
CFC114	−0.014 to 0.024	0.007	0.012 ± 0.022	0	3.6[g]	NR	
Halon-1211	−0.010 to 0.001	−0.005	−0.01 ± 0.52	0.01	5.4[g]	NR	
Halon-2402	−0.0027 to −0.0001	−0.0003	−0.0010 ± 0.0021	−0.0001	5.4[g]	NR	
			Halocarbons				
CH_3Cl	**−0.58 to 2.6**	**1.2**	**2.3 ± 2.3**	**2.1**	10[d]	**180 ± 110**	**paddy**
CH_3Br	**−0.01 to 0.80**	**0.50**	**1 ± 0.2**	**0.1**	10[d]	**2.3**	**rice**
CH_3I	**0.07 to 28.**	**12**	**30.8 ± 4.4**	**0.3**	14[d]	**0.8**	**rice**
CH_2Cl_2	<0.39	<0.39	<0.94		10[g]	NR	
CH_2Br_2	−0.015 to 0.006	−0.002	−0.004 ± 0.014	0.003	10[g]	NR	
$CHCl_3$	−0.033 to 0.080	0.047	0.065 ± 0.097	0.033	10[g]	NR	
$CHBr_3$	**0.012 to 0.032**	**0.021**	**0.025 ± 0.013**	**0.014**	11[g]	**NR**	**paddy/rice**
$CHBrCl_2$	**−0.0001 to 0.0045**	**0.0019**	**0.0029 ± 0.0022**	**0.0005**	11[g]	**NR**	**paddy**
CCl_4	0.003 to 0.061	0.022	0.034 ± 0.045	0.031	3.2[g]	NR	
C_2Cl_4	0.04 to 0.43	0.20	0.23 ± 0.12	0.17	10[g]	NR	
C_2H_5Cl	**0.02 to 0.56**	**0.35**	**0.60 ± 0.50**	**0.88**	20[d]	**NR**	**paddy**
CH_3CCl_3	0.05 to 0.65	0.21	0.28 ± 0.32	0.27	5.1[g]	NR	
Nitrogen Compounds							
			Alkyl nitrates				
CH_3ONO_2	−0.0009 to 0.0049	0.0013	0.0027 ± 0.0054	0.0038	20[h]	NR	
$C_2H_5ONO_2$	**0.011 to 0.11**	**0.035**	**0.070 ± 0.042**	**0.069**	20[h]	**NR**	**photochem**
i-$C_3H_7ONO_2$	**0.043 to 0.31**	**0.095**	**0.21 ± 0.13**	**0.18**	20[h]	**NR**	**photochem**
n-$C_3H_7ONO_2$	**0.005 to 0.071**	**0.020**	**0.061 ± 0.049**	**0.025**	20[h]	**NR**	**photochem**

Table 1. (continued)

	Instantaneous Emissions		Integrated Seasonal Emissions				
Compound	Range of Emissions, $\mu g \; m^{-2} \; hr^{-1}$	Median Emission, $\mu g \; m^{-2} \; hr^{-1}$	Planted Chambers, $mg \; m^{-2}$	Control Chambers, $mg \; m^{-2}$	Accuracy of reported value, $\pm\%$	Biomass Burning, $mg \; m^{-2b,c}$	Likely Region of Origin for Compound
$2\text{-}C_4H_9ONO_2$	**−0.002 to 0.13**	**0.043**	**0.066 ± 0.056**	**0.036**	**20[h]**	**NR**	**photochem**
Sulfur Compounds						0	
CH_3SCH_3	**0.5 to 17**	**6.5**	**15 ± 4**	**0.3**	**11[i]**	**NR**	**rice**

All compounds with reported instantaneous emissions were measured during this study. All other compound emissions and biomass burning values are estimated, and references are listed accordingly; for explanations regarding the "Likely Region of Origin," see text.

[a]Boldfaced values denote compounds whose emissions are statistically different from zero and from the control (over glass) chamber emissions.

[b]Values are from agricultural residue estimates by *Andreae and Merlet* [2001] assuming a dry biomass weight of 750 g m^{-2}.

[c]NR indicates that the value was not reported.

[d]Standard is obtained from Scott Specialty Gases, Inc. Usual standard accuracy is ±10%.

[e]Standard is based on quantification of equivalent carbon. Standard accuracy is ±10%.

[f]Value is estimated from *Guenther et al.* [1995]; see text.

[g]Standard was prepared gravimetrically and diluted when necessary. Standard accuracy ranges from ±2 to 10%.

[h]Standard obtained from the National Center for Atmospheric Research. Standard accuracy is ±20%.

[i]Quantification is based on isotopic mass ratio spectroscopy. Accuracy is ±10%.

used as a control plot, where the field was flooded but no rice was grown. Samples were taken from planted ($n = 3$) and control ($n = 1$) chambers at each sampling period.

[13] Our chamber measurements relied on stable chamber bases, which were 0.3-m inner diameter PVC rings that were maintained above the soil with aluminum poles. They were placed so that after flooding, the field water reached midbase (~10 cm water depth). During the season, transparent, polycarbonate, cylindrical sections, 30 cm in height, were placed on the bases, creating a diffusion seal between the bases and the extensions and a water seal at the base-water interface. A transparent polycarbonate lid was placed on the chamber, isolating the interior air. Additional chamber extensions, 0.3 m in height, were added as rice height increased over the season.

[14] The polycarbonate extensions were transparent to UV and visible light and allowed ~65–70% of irradiant light into the chamber. An aluminum-wrapped copper coil

Figure 1. Houston 2000 field setup. Survey samples described were taken from the circular chambers, described in the figure as the "transparent methyl halide sampling chamber." Methyl and ethyl halide samples were taken from the transparent chambers as well, while methane samples were taken from the opaque, aluminum, square chambers. Note that the figure is not to scale.

inside the chamber, through which ice water was flushed during measurements, ameliorated the effects of evapotranspiration and irradiant light. In this way chamber temperatures rarely passed beyond 35°C, and the maximum inner chamber temperature did not exceed 40°C. These temperatures were common in the ambient air over the Houston paddies during the growing season (Figure 2). The minimum chamber volume with one extension was 30 L. Our maximum sampling volume during a single chamber placement was 1.1 L, a little over 3% of the minimum total chamber volume. Methane chambers were 0.6×0.6-m opaque aluminum boxes [*Sass et al.*, 2002].

[15] PVC chamber bases and extensions were extensively tested for emission or uptake of methane and/or methyl halides and appeared to be neutral for these compounds. To test chamber stability for the other compounds detailed in this study, we placed chamber bases and extensions over a glass plate in full sunlight and allowed the chambers to equilibrate for 10 minutes (3 control replicates). As in the field, chamber samples were taken at 0 and 10 min (internal chamber temperatures were 40°C). The flux (when measurable) was compared to emission rates observed in the field.[1] If field emissions were within 1 standard deviation of the control chamber emissions over glass, we assumed chamber contamination and labeled these results appropriately (the only affected compounds were alkanes)[1].

[16] Air samples were drawn from the chamber into electropolished stainless steel canisters (previously evacuated to 1×10^{-2} torr) through a silica-coated stainless steel line immersed in an ice bath. The ice bath maintained all samples at a consistently arid relative humidity (RH) (100% RH at 0°C). Electropolished stainless steel canisters were either 0.5 L or 2 L in volume and were analyzed within ten days of sampling. Samples were stored at room temperature (20°–22° C) before sampling.

[17] Field samples were taken at 0, 5, and 10 min. Zero-minute samples were taken outside of the chamber, 1 m over the surface of the rice paddy, and acted as ambient air samples as well as initial chamber concentrations. Methane and methyl halide samples were taken once before flooding (44
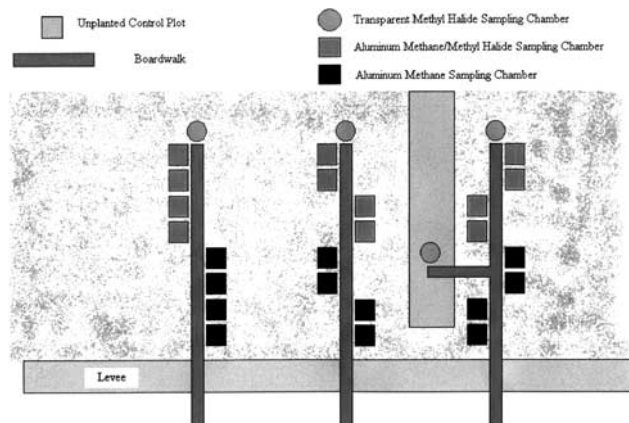
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[1] Supporting data tables are available at ftp://ftp.agu.org/apend/jd/2002jd002814.
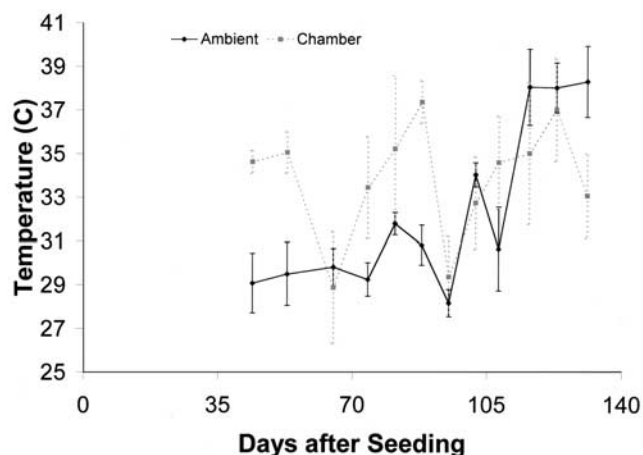
Figure 2. Ambient and final chamber temperatures for the Houston field campaign, 2000. Chamber temperatures will, at any given time, represent a value between the ambient and the final chamber temperature. Error bars represent standard deviation of all ambient and final chamber temperatures for each day.

days after planting) and approximately once a week thereafter for the duration of the growing season (last sampling 131 days after planting). Survey samples were analyzed for a subset of these dates (between 65 and 108 days after planting). The samples were transported to either the Cicerone laboratory or the Rowland/Blake laboratory at the University of California, Irvine, where they were analyzed.

2.3. Sample Analysis

[18] Surveys of emissions are difficult to obtain owing to chromatographic column separation and detector sensitivities over the full spectrum of potential compounds. Hydrocarbon species may be detected with flame ionization detectors (FIDs); however, their ability to detect halocarbons is limited. Likewise, halocarbons may be easily detected using electron capture detectors (ECDs), but ECDs are much less sensitive to hydrocarbons. Mass spectrometers may be used to survey broad ranges of masses, but scanning of this type provides less sensitivity than specific mass detection. Our analytical system involves cryogenic preconcentration of 220 cm^3 of air in a 0.64-cm OD stainless steel loop filled with glass beads immersed in a liquid nitrogen bath ($-196°C$). The preconcentrated sample is vaporized in a hot water bath ($95°-100°C$) and split into five streams directed to three separate gas chromatographs (GC) (Hewlett-Packard 6890). The first GC is equipped with two different detector/column combinations; a 60-m, 0.32-mm ID, 1-μm thickness, 1701 Restek column output to an ECD along with a GS-Alumina PLOT, 30-m, 0.53-mm ID column (J & W Scientific) attached to an FID. The second GC is equipped with a 60-m, 0.32-mm ID, 1 μm thickness, DB-1 column (J & W Scientific) output to an FID. The third GC is also equipped with two separate column/detector combinations; the first is a 60-m, 0.25-mm ID, 0.5 μm thickness, DB-5-MS column output to an quadrupole mass spectrometer detector (HP-5973) working in selected ion monitoring mode. The output of the MS is connected to a 5-m, 0.25-mm ID, 0.5-μm thickness, 1701

Restek column output to an ECD. See *Colman et al.* [2001] for a more complete description of the instrumental methods. Concentrations of methane and methyl halides were determined using the methods described by *Sass et al.* [2002] and *Redeker et al.* [2000].

[19] Standards for each gas and the overall accuracy of the measurements are listed in Table 1. Overall accuracy is calculated as the square root of the square of the method precision plus the square of the standard accuracy. Stock standards were generally prepared gravimetrically then diluted to appropriate standard concentrations, either in the lab or by commercial (Scott Specialty gases) or scientific (National Center for Atmospheric Research) suppliers. Gas standards were not run with humidification.

2.4. Seasonal Flux Calculation

[20] Seasonal integrated totals were calculated via trapezoidal integration, with days 45 and 140 assumed to be the beginning and the end of the season, corresponding to flooding and harvest. Emissions in this study were assumed to be zero at each end point owing to the observed sensitivity of methane and methyl halide emissions to soil water saturation. When the soil is dry, before flooding and after harvest, anaerobic conditions in the soil column are not available in sufficient amounts to allow for significant production of methane. Likewise, although for reasons that are at this time not well understood, methyl halide emissions are nearly zero before flooding [*Redeker et al.*, 2002] and are observed to decrease to nearly zero in other fields after harvest [*Redeker et al.*, 2000]. As the water column is not in place during these times, and the associated water algae and water plants are not growing, it is likely that emissions from these sources would also be minimal. Photochemistry that relies on dissolved biological organic material would be curtailed during these times, leaving only aerobic subsurface bacteria and biomatter-degrading surface bacteria and fungi as potential emitters of compounds to the atmosphere. We expect that, if anything, we underestimate emissions of some compounds slightly over the course of the season.

3. Results and Discussion
3.1. Hydrocarbon Emissions
3.1.1. Methane

[21] Irrigated rice agriculture is a rich source of methane; knowledge of the processes governing methane has been reviewed a number of times [*Cicerone and Oremland*, 1988; *Neue*, 1993; *Neue and Sass*, 1994]. Methane emissions from rice fields result from archeabacterial processes: production in flooded anaerobic microsites and consumption (oxidation) in aerobic microsites. Flooding rice fields reduces soil oxygen and promotes anaerobic fermentation of carbon supplied by rice plants and other incorporated organics. The end product of these processes is the formation of methane. Methane reaches the atmosphere by ebullition of gas bubbles, by diffusion, and through a gas-conducting system in rice plants. These processes are governed by an array of factors linking the physical and biological characteristics of flooded soil environments with specific agricultural management practices.

[22] The seasonal development of observed methane emissions is shown in Figure 3. It is similar to methane emissions observed from many other irrigated rice fields
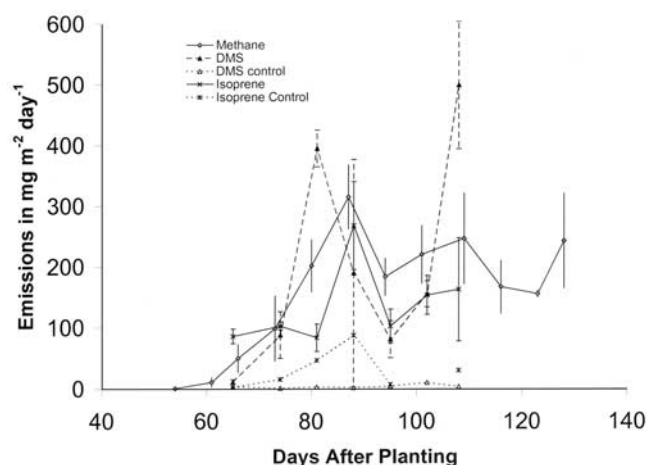
Figure 3. Isoprene, DMS, and methane emissions from Houston Fields. DMS and Isoprene emissions are multiplied by 1000, to scale with methane emissions. Error bars show 1 standard deviation.

worldwide [*Sass et al.*, 2002]. The average seasonal emission value of this site was 12 ± 1.7 g m^{-2}. Methane flux was negligible for the first week of flooding, gradually increased until heading, decreased slightly immediately afterward, and remained nearly constant until the end of the season. The decrease in methane emission that started during heading of the rice plants may be due to additional carbon use required by the developing panicles and grain. This developmental change would result in a decrease in carbon allocation to the root system and consequently to the soil bacteria, causing the methane production to be lowered. A smaller emission peak near anthesis was unanticipated but apparently real since it appears in each of 24 replicate plots (Figure 1). This is also true of an additional emission peak very near the end of the flooded part of the season. This increase in methane emission may be due to the observed senescence of the rice plants and loss of leaves and subsequent decay in the floodwater and soil.

3.1.2. Nonmethane Alkanes

[23] *Khalil et al.* [1990] reported instantaneous emission rates that ranged from -0.6 to 0.9 (ethane), 0.2 to 1.3 (propane), -0.6 to 1.2 (*i*-butane), and -0.2 to 0.5 (*n*-butane) μg m^{-2} hr^{-1} in flooded Asian rice paddy fields during two sampling periods in the early and late stages of growth (all *Khalil et al.* [1990] data are from the same conditions). Our observed rates for these compounds ranged from 0.6 to 2.7 (ethane), -0.1 to 1.3 (propane), -0.6 to 0.6 (i-butane), and -3.7 to 0.7 (n-butane) μg m^{-2} hr^{-1} during the late vegetative through early ripening stages of growth. We did not observe distinct ethane, propane, butane, pentane, or heptane emissions from the fields in Houston. While integrated seasonal emissions were positive (0.1 to 1.8 mg m^{-2}), the averaged fluxes were statistically inseparable from 0 for all gases (Table 1).[1] The flux of alkanes from the control chamber tested over glass was, within 1 standard deviation, the same as the observed emissions from field chambers for ethane, propane, and butane. That the observed alkane emissions correspond well to previously published data suggest that previous results may have also been contaminated through sampling methods.

[24] Hexane is the only nonmethane alkane that showed a clear emission from rice paddies during this study. The integrated seasonal flux is nearly 2 standard deviations from 0 (0.23 ± 0.12 mg m^{-2}), and there were no observed contaminations from the sampling chamber or canisters. Maximum hexane emissions occurred during the late vegetative stage and decreased through the reproductive stage into ripening. Sampling chamber temperatures do not correspond well to hexane emissions (Table 2). This pattern would suggest that hexane emissions may be linked to vegetative stage processes in the rice plant. Integrated emissions from the unplanted control plots in Houston are similar to planted plot emissions (0.14 mg m^{-2}, Table 1), however; if fluxes of hexane are linked to the vegetative stage, then plant-based processes may exert some control over emissions. We tentatively assign both rice-mediated and paddy-based mechanisms for hexane release.

3.1.3. Alkenes and Ethyne

[25] While there were no discernible fluxes of the triple-bonded ethyne from Houston rice paddies, we did observe fluxes of ethene, propene, and several butene isomers from both planted and unplanted regions in the field. *Khalil et al.* [1990] reported instantaneous emissions for alkenes that ranged from 0.1 to 1.1 (ethane), -0.5 to -0.1 (ethyne), and -0.2 to 1.9 (propene) μg m^{-2} hr^{-1}. Our instantaneous emissions ranged from 3.2 to 6.2 (ethene), -0.01 to 0.08 (ethyne), and 1.5 to 2.8 (propene) μg m^{-2} hr^{-1}, as well as 0.5 to 2.3 and 0.5 to 1 μg m^{-2} hr^{-1} for 1-butene and trans-2-butene (Table 1).[1] Cis-2-butene was only detected between day 60 and 80, while chamber air samples taken between days 80 and 110 were below the detection limit.

[26] Alkenes are known to be photochemically produced in organically rich seawater by UV and short visible range sunlight [*Ratte et al.*, 1998]. The Houston rice paddies, and flooded rice paddies in general, are organically rich waters with intensive algal growth throughout the water column. Water columns in rice paddies are also likely to be at least semibrackish water (0.5–5‰) which would provide anions and cations for photochemical reaction stabilization (K. R. Redeker et al., unpublished data, 2002).

[27] The ratio of ethene to propene emissions further corroborates that photochemistry is the driving mechanism behind alkene production in the rice paddy water column. Photochemically driven ethene production has been measured in laboratory experiments to be twice that of propene [*Ratte et al.*, 1998]. Relative emissions of butene are, as of yet, unreported, but our results suggest that the relative rates of production will be 1:2:4:8 for ethene, propene, 1-butene, and trans-2-butene.

[28] The standard sampling chambers used in the *Khalil et al.* [1990, 1998] studies are opaque frames that would arrest photochemistry within the chamber. Our chambers, while not 100% transparent (see methods), allow incoming short-wave radiation, which may explain the discrepancies between the two sets of measurements. As our chambers do absorb/scatter some of the incoming radiation, we may infer that measured emissions from Houston are underestimations.

3.1.4. Monoterpenes and Isoprene

[29] Isoprene emissions in Houston were strongly influenced by the presence of rice plants, with integrated seasonal fluxes from planted chambers of 8.9 ± 2.7 mg m^{-2}. The unplanted control produced 20% of the isoprene

Table 2. Correlations (R) for Gases Emitted From Houston Rice Paddies[a]

	Methane	Hexane	Ethene	Propene	1-butene	t-2-butene	Isoprene	Benzene	CH_3Cl	CH_3Br	CH_3I	$CHBr_3$	$CHBrCl_2$	C_2H_5Cl	$EtONO_2$	$i\text{-}PrONO_2$	$n\text{-}PrONO_2$	$2\text{-}BuONO_2$	DMS
Field temperature	0.28	**-0.90**	0.35	0.49	0.10	-0.20	0.26	**0.68**	0.14	-0.20	-0.45	-0.45	-0.36	-0.17	0.39	0.39	0.37	0.48	0.33
Chamber temperature	0.33	-0.33	-0.20	-0.40	0.10	**-0.97**	**0.67**	-0.14	0.17	-0.10	0	0	**0.66**	0.30	-0.10	0	0.10	0.10	0.62
Methane		-0.68	0.20	-0.24	0	-0.41	**0.81**	0.10	**0.54**	**0.52**	0	-0.26	**0.55**	0	-0.14	-0.10	0.10	-0.10	**0.55**
Hexane			-0.62	-0.42	-0.24	0.10	-0.50	-0.57	-0.56	-0.32	0	0.53	0.20	-0.17	-0.28	-0.24	-0.32	-0.42	-0.30
Ethene				0.69	-0.48	0.62	0.14	**0.70**	0.14	-0.26	**-0.79**	-0.62	0.26	0	0.26	0.20	**0.84**	0	0.36
Propene					0.10	0.57	-0.10	**0.83**	0	0.30	-0.61	-0.17	**-0.75**	0.20	**0.85**	**0.80**	**0.81**	0.67	-0.22
1−butene						-0.24	0.36	-0.26	-0.37	**0.96**	0.56	**0.82**	0	-0.30	0.54	0.58	-0.22	**0.73**	**-0.82**
t-2-butene							0.48	0.55	-0.49	-0.14	**-0.98**	-0.20	-0.72	**-0.84**	0.32	0.24	0.32	0	-0.57
Isoprene								-0.20	0.20	0.49	0.26	0.20	0.63	0.22	0.51	0.10	0.14	0.14	0.17
Benzene									0.45	0.14	**-0.70**	-0.63	**-0.81**	0.50	0	0.45	0.63	0.35	0.24
Methyl chloride										**0.63**	0.46	-0.66	0	**0.66**	0.49	0	0.24	0	**0.79**
Methyl bromide											0.64	**0.76**	-0.10	0.20	-0.17	0.55	0.22	0.48	0
Methyl iodide												0.57	0.53	0.22	0.32	-0.10	-0.57	0.14	-0.20
$CHBr_3$													0.20	-0.42	-0.63	0.39	-0.28	0.44	**-0.81**
$CHBrCl_2$														-0.40	0.22	-0.57	-0.32	-0.51	0.32
C_2H_5Cl																0.24	0.32	0.20	0.57
$EtONO_2$																**0.99**	0.62	**0.93**	-0.41
$i\text{-}PrONO_2$																	0.61	**0.94**	-0.13
$n\text{-}PrONO_2$																		0.39	0.26
$2\text{-}BuONO_2$																			-0.50

[a]Negative values indicate negative correlations. Boldfaced values are statistically significant (confidence >95%).

emitted by the planted plots (1.7 mg m^{-2}) (Table 1 and Figure 3). Emissions from unplanted regions may be due to water column algae, as isoprene emissions from marine algae have been measured [Shaw, 2001]. Although maximum emissions occurred just after heading, any developmentally driven emission pattern is uncertain at this point.

[30] Guenther et al. [1995] estimated rice paddy emissions of isoprene to be 5.7 μg g^{-1} biomass hr^{-1} based on measured rates from other crops and grasses. A conservative dry biomass density for rice paddies during the late season would be 0.8 kg m^{-2} (M. D. Summers et al., available at http://www.bioproducts-bioenergy.gov/pdfs/bcota/abstracts/1/305.pdf, 2002), which would give an emission rate of 4500 μg isoprene m^{-2} hr^{-1}. Our results do not support this value; our best estimate for average isoprene emissions is 3 orders of magnitude smaller at 3.7 μg m^{-2} hr^{-1}. As the emissions from rice estimated by Guenther et al. [1995] are extrapolations based on emissions from other crops, it is not surprising that the measured values and the estimated values are different. While the large discrepancy is surprising, it may be due to the unusual nature of rice, which is grown in flooded conditions.

[31] The ratio of isoprene to monoterpene emissions described by Guenther et al. [1995] allows us to generate an order of magnitude estimate of monoterpene emissions based on measured isoprene emissions. This calculation gives an average rice paddy monoterpene emission rate of 0.15 μg m^{-2} hr^{-1} and a seasonal integrated emission of 0.35 mg m^{-2}.

[32] Prior studies that attempted to measure isoprene, monoterpenes, and other hydrocarbon emissions from rice and other crops [Lamb et al., 1987; Winer et al., 1992] were unable to quantify isoprene emissions. They may have been unable to detect isoprene emissions owing to instrumental sensitivity. Their listed limits of detection were near 1 μg g^{-1} hr^{-1} [Lamb et al., 1987] and 0.008 μg g^{-1} hr^{-1} [Winer et al., 1992]. An estimate of these studies' sensitivity to isoprene emissions from rice paddies using 0.8 kg biomass m^{-2} suggests instrumental limits of detection near 800 μg m^{-2} hr^{-1} and 6.5 μg m^{-2} hr^{-1}, respectively. Sampling days with emissions larger than 6.5 μg m^{-2} hr^{-1} occurred only twice during the 2000 study. As both the Lamb et al. [1987] and Winer et al. [1992] studies performed only a few measurements over a limited time span (less than a week), it is highly unlikely that they would have detected isoprene.

3.2. Chlorofluorocarbon and Halocarbon Emissions
3.2.1. CFCs
[33] Khalil et al. [1990] suggested rice fields could potentially act as a global sink for anthropogenic halocarbons. Emission/consumption rates of these gases were statistically identical to zero during this study (Table 1 and Figure 4)[1]. Instantaneous emissions ranged between 0.01 and 0.21 (CFC-11, CCl_3F), -0.6 and 3.5 (CFC-113, $C_2Cl_3F_3$), -0.014 and 0.024 (CFC-114, $C_2Cl_2F_4$), 0.06 and 0.30 (CFC-12, $C_2Cl_2F_2$), -0.010 and 0.001 (Halon-1211, $CBrClF_2$), and -0.0027 and -0.0001 (Halon-2402, $C_2Br_2F_4$) μg m^{-2} hr^{-1} during the 2000 Houston season (Table 1). The reported average instantaneous emissions from Khalil et al. [1990] are -0.2 and -0.08 μg m^{-2} hr^{-1} for CFC-11 and CFC-12. A later study by Khalil et al. [1998] showed a range of measured fluxes for CFC-11 and
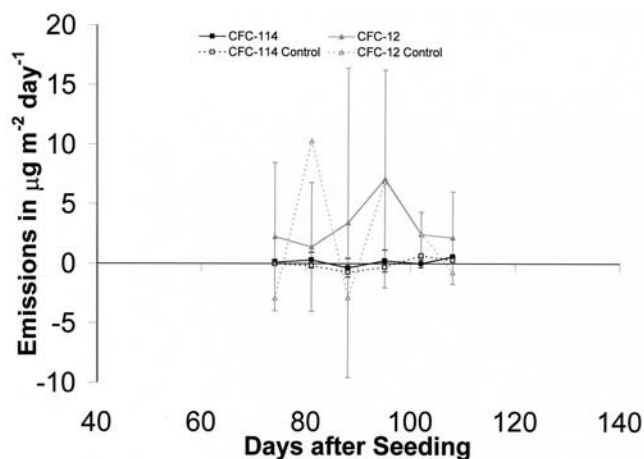
Figure 4. Representative CFC emissions from Houston Fields. Error bars show 1 standard deviation ($n = 3$).

CFC-12 over several seasons. Both gases show uptake in the first season, emission in the second, and indeterminant emissions in the third. In our study, there was no evidence to suggest that rice paddies acted as either a source or a sink for CFCs or Halons (Figure 4 and Table 1)[1].

3.2.2. Halocarbons

[34] We have reported previously [*Redeker et al.*, 2000, 2002] that rice paddies emit methyl halides. It is also apparent that the processes that drive emission of methyl chloride (CH_3Cl) from rice paddies are not the same as those that drive the emissions of methyl bromide (CH_3Br) and methyl iodide (CH_3I) (Redeker and Cicerone, submitted manuscript, 2003). Methyl iodide emissions are strongest during the vegetative stage of rice development, while methyl bromide emissions are strongest during the reproductive stage [*Redeker et al.*, 2000, 2002]. Integrated seasonal emissions of methyl chloride, methyl bromide, and methyl iodide at Houston were 2.3 ± 2.3, 1 ± 0.2, and $31. \pm 4$. mg m^{-2} [*Redeker et al.*, 2002] (Figure 5). As reported by *Redeker et al.* [2002], methyl iodide and methyl bromide emissions were mediated by rice while flux of methyl chloride was unaffected by plant presence.

[35] *Khalil et al.* [1990, 1998] reported rice paddy emission of chloroform ($CHCl_3$), emission and uptake of carbon tetrachloride (CCl_4), and emission and uptake of methyl chloroform (CH_3CCl_3) from flooded Asian rice paddies [*Khalil et al.*, 1990, 1998]. Houston rice paddies did not significantly consume or emit any of these compounds (Table 1). Previously reported fluxes ranged from 0.1 to 3.3 ($CHCl_3$), -0.10 to 0.25 (CCl_4), and -0.1 to 0.2 (CH_3CCl_3) µg m^{-2} hr^{-1} while Houston emissions ranged from -0.033 to 0.080 ($CHCl_3$), 0.003 to 0.061 (CCl_4), and 0.05 to 0.65 (CH_3CCl_3) µg m^{-2} hr^{-1} (Table 1).

[36] The differences in observed fluxes may be due to the number of sampling sites used in each experiment. We have shown that measured methyl halide emissions are not likely to be accurate within 20% (at the 95% confidence level) in experiments with fewer than three sampling sites [*Redeker et al.*, 2002]. The *Khalil et al.* [1990, 1998] studies used two chambers, which may have introduced a spatial variability error into their analysis. Our measurements in Houston were based on three chamber placements. Alternatively, enclo-

sure time may have influenced the results through decreased plant activity due to opaque chambers or decreased carbon dioxide concentrations. Our chamber placements at Houston were in transparent chambers for a maximum of 10 min, while the previous studies maintained an enclosed system for up to 90 min. Finally, field to field variability cannot be ruled out as a possible explanation given the many different field conditions between Asian and Houston rice paddies.

[37] We detected only a few, nonmethyl halide, halocarbons emitted from rice paddies. Two of these were the polyhalogenated compounds: bromoform ($CHBr_3$); and dichlorobromomethane ($CHBrCl_2$). Polyhalocarbon production from marine algae has been reported previously [*Carpenter and Liss*, 2000; *Manley and Barbero*, 2001; *Plummer and Edzwald*, 2001]. When the nearly equivalent emissions from the unplanted controls are considered, along with the heavy water column algal population, it seems plausible to suggest that polyhalogenated compounds are produced by algae in the water column. Instantaneous emissions of bromoform and dichlorobromomethane ranged from 0.012 to 0.032 and -0.0001 to 0.0045 µg m^{-2} hr^{-1}, respectively, with median fluxes of 0.021 and 0.0019 µg m^{-2} hr^{-1}.

[38] Ethyl chloride (C_2H_5Cl), like methyl chloride, was a product of the rice paddy environment itself (Figure 5). We deduce this from the nearly equivalent emissions from unplanted paddy regions as compared to planted paddy regions. The absence of emissions prior to field flooding (Figure 5) suggests that soil processes did not strongly influence the production of ethyl chloride. We are the first to report this compound as a natural product from terrestrial ecosystems. Integrated seasonal emissions were 0.60 ± 0.50 mg m^{-2} with emissions from unplanted control chambers of 0.88 mg m^{-2} (Table 1, Figure 5). Instantaneous emissions ranged from 0.02 to 0.56 µg m^{-2} hr^{-1}.

3.3. Sulfur Compound Emissions

[39] Rice mediated emissions of dimethyl sulfide (DMS) (CH_3SCH_3) have been reported previously for Asian rice paddies studied through multiple chamber placements over several annual cycles [*Kanda et al.*, 1992; *Minami*, 1994; *Nouchi et al.*, 1997; *Yang et al.*, 1998]. In these studies,
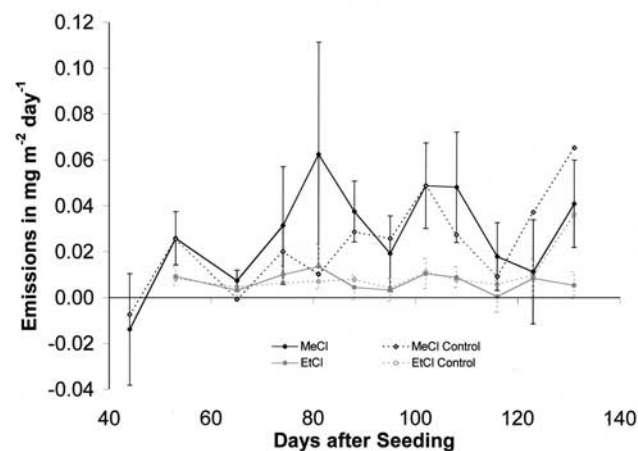

Figure 5. Emissions of methyl and ethyl chloride from Houston Fields. Error bars show 1 standard deviation ($n = 3$).

emission of DMS after the growing season was significant and was accounted for in the annual total. Integrated annual emissions ranged from 5.6 to 15 mg m^{-2} as compared to the growing-season-only seasonal total from Houston of 15 $\pm$ 4 mg m^{-2}. As our results do not include preseason and postseason emissions, we expect that Houston rice paddies would emit more dimethyl sulfide than the rice paddies previously observed. These annual emissions are comparable to other flooded and/or grassy ecosystems, including maize and wheat fields (5 mg m^{-2}), mangrove lagoons (22 mg m^{-2}), and freshwater marsh grasses (9 mg m^{-2}) [*Kanda et al.*, 1995; *Hines et al.*, 1993].

[40] Instantaneous emissions from prior studies on rice paddies range from 1 to 15.5 μg m^{-2} hr^{-1} [*Yang et al.*, 1998]. Houston planted plot emissions ranged from 0.5 to 17 μg m^{-2} hr^{-1} as compared to unplanted regions where the maximum seasonal DMS flux was 0.4 μg m^{-2} hr^{-1} (Figure 3). While DMS emissions appeared to maximize near heading (in agreement with *Minami* [1994], *Nouchi et al.* [1997], and *Yang et al.*, 1998), they were not obviously correlated with any growth stage and in fact achieve maximum emissions both before heading and after the initiation of ripening.

[41] Studies from Asian rice paddies indicate that soil processes play no significant role in the production of DMS [*Nouchi et al.*, 1997; *Yang et al.*, 1998], while others indicate that under dry, unplanted conditions, paddy fields can produce DMS [*Kanda et al.*, 1992; *Minami*, 1994]. It is still unclear whether the DMS generated in Houston was produced in the soil and transported via the rice plant (as is methane; see Figure 3) or whether it was produced by the rice plant itself, especially since studies have shown that microbial degradation of biological material under anoxic, organically rich soil conditions (peat bogs) can produce DMS [*de Mello and Hines*, 1994; *Kiene and Hines*, 1995].

3.4. Nitrogen Compound Emissions

[42] Alkyl nitrates (C$_x$H$_{2x+1}$ONO$_2$) are suspected to be produced photochemically in organically rich water. Recent laboratory results have shown that this mechanism is feasible [*Dahl et al.*, 2002]. Regions of upwelling, nutrient-rich, and therefore nitrate-rich, tropical ocean waters are found below spikes in ambient alkyl nitrate concentrations; however, the mechanism for production in these waters is not yet certain [*Atlas et al.*, 1993; *Blake et al.*, 1999].

[43] As expected for photochemically produced compounds, alkyl nitrate emissions were not influenced by the presence of rice or the stage of rice growth. While there were no discernible emissions of methyl nitrate (CH$_3$ONO$_2$) instantaneous fluxes ranged from 0.01 to 0.11 (ethyl nitrate, C$_2$H$_5$ONO$_2$), 0.04 to 0.31 (*i*-propyl nitrate, C$_3$H$_7$ONO$_2$), 0.005 to 0.071 (*n*-propyl nitrate, C$_3$H$_7$ONO$_2$), and -0 to 0.13 (2-butyl nitrate, C$_4$H$_9$ONO$_2$) μg m^{-2} hr^{-1} with median fluxes of 0.035, 0.095, 0.020, and 0.043 μg m^{-2} hr^{-1}, respectively, for each. These are the first alkyl nitrate flux measurements reported for a natural terrestrial ecosystem. While the evidence reported in this study suggests a photochemical or photochemically initiated production pathway, biological production in the water column cannot be removed as a possibility.

3.5. Flux Correlations

[44] Correlations between emitted compounds and between emissions and chamber temperatures can provide information regarding the likely source of each compound. Our calculated correlation coefficients (R) are listed in Table 2. A more comprehensive statistical analysis of this data set would be inappropriate, as the number of variables is far greater than the number of possible samples (generally $n = 6$ in this study with a maximum n of 18). Two cautions: there are a limited number of samples, which limits the obtainable information, and there is a 5% chance within this technique that any statistical correlation observed will be purely stochastic in nature.

[45] The values used to calculate correlation coefficients are average values for the three planted chamber emplacements from each sampling day. This leads to a seasonal total of 12 daily averages for the methyl halides, ethyl chloride, and methane and 6 daily averages for the rest of the compounds studied. The effect of averaging daily fluxes on correlation coefficients can be seen when these correlations are compared to correlations generated from the complete data set for methyl halides [*Redeker et al.*, 2002]. The highly variable emissions of methyl chloride, when averaged, are consistently more correlated (R increases by an average of 0.14) with methane, methyl bromide, and methyl iodide. Even when averaged, there are only six compounds that are correlated with methyl chloride above our threshold value of 0.5, and of those, only one is correlated beyond 0.75, which suggests that the additional weighting from averaging will not severely influence the results listed here for highly variable compounds. The less variable methane, methyl bromide, and methyl iodide emissions are nearly unchanged (R increases by an average of 0.02).

3.5.1. Gas Flux Correlations to Ambient and Chamber Temperatures

[46] The ambient field temperatures and the chamber temperatures for all sampling dates are shown in Figure 2. Ambient field temperatures remained low (30°C) through tillering, heading, and flowering and then increased to seasonal highs of 39°C during ripening. Chamber temperatures varied with irradiant light and were sensitive to sensible heat loss from the paddy, leading to internal chamber temperature fluctuations over the course of the season between 29° and 38°C, with an average value of 34°C. Since the amount of sunlight changed rapidly during the course of sampling, the internal chamber temperatures often did not reflect the amount of irradiant light just prior to or during the sampling period. Also, ambient air temperatures were more likely to reflect field water temperatures than internal chamber temperatures, which changed rapidly within a few minutes.

[47] Ambient air temperatures did not correlate well with many of the observed emissions from Houston. Benzene was the only compound to have a positive correlation >0.5. Oddly, hexane had a highly negative correlation with ambient air temperatures (−0.90). Both of these correlations are statistically significant at 5% confidence (Table 2). Internal chamber temperatures were also poorly correlated with many of the observed fluxes (Table 2). The only compound significantly positively correlated with internal chamber temperature was isoprene. Isoprene is known to be affected by temperature increases [*Monson et al.*, 1995;

Yang et al., 1998]. Methyl bromide and methyl iodide (correlations of −0.10 and 0 in this study) have since been shown to be very sensitive to internal chamber temperatures under more controlled conditions (Redeker and Cicerone, submitted manuscript, 2003), which may indicate that other compounds are more sensitive to temperature than are indicated here.

[48] Trans-2-butene had a very strong negative correlation with internal chamber temperatures (−0.97), which was unexplainable through results from this study. For both internal and ambient temperatures the negative correlations were more significant than the positive correlations. At this time we do not have a compelling explanation for this phenomenon.

3.5.2. Gas-to-Gas Flux Correlations

[49] Correlation coefficients (R) are listed in Table 2. Methane emissions were driven by microbiological production within the soil column and were then, principally, transported through the rice plant to the atmosphere [*Wang et al.*, 1997; *Khalil et al.*, 1998]. It is possible that DMS production was microbiological in origin and that this was the driving mechanism behind the correlation of these gases ($R = 0.55$) (Table 2 and Figure 3). Isoprene emissions correlated with methane reasonably well ($R = 0.67$) (Figure 3). While the microbial community cannot be discounted, it would be surprising if methane and isoprene were produced together in the soil, as the observed isoprene emissions are more likely to be explained through rice plant and water column algal production mechanisms [*Monson et al.*, 1995; *Shaw*, 2001]. Isoprene emissions are poorly correlated with all other compounds (<0.50).

[50] Within our study, hexane emissions were poorly correlated with all other gases ($R < 0.6$). The most striking correlation between gases was the strong positive correlation between alkene and alkyl nitrate emissions. The overall correlated nature of alkenes and alkyl nitrates suggests either that they are produced in a similar fashion or that alkyl nitrates are formed from alkenes in the water column after they are produced. Ethene, propene, t-2-butene, and benzene correlated positively with most other alkenes (range 0.55 to 0.83), although only the benzene/propene correlation is statistically significant. One-butene did not correlate well with other alkene emissions but did appear to positively correlate with methyl bromide (0.96) and bromoform (0.82). Emissions of ethene, propene, 1-butene, and benzene correlated well with alkyl nitrate fluxes (range 0.51 to 0.85), with significant correlations between propene and ethyl, isopropyl, and *n*-propyl nitrates. Ethene correlated significantly with *n*-propyl nitrate, while 1-butene correlated well with 2-butyl nitrate ($R = 0.73$). In general, alkene emissions appear to be inversely proportional to methyl iodide (range −0.61 to −0.98) and $CHBrCl_2$ production (range −0.72 to −0.81). Both butenes are negatively correlated with DMS (t-2-butene: −0.57; 1-butene: −0.82). Very strong correlations were found between ethyl, isopropyl, and 2-butyl nitrate emissions (range 0.93 to 0.99), suggesting similar production mechanisms. If we assume that most alkenes were produced photochemically, we can then tentatively identify alkyl nitrates as compounds that were produced or initiated photochemically as well. Production of 1-butene did not appear to be primarily photochemically driven and could have been plant generated; it may however, have acted

as a precursor to other photochemically generated gases such as 2-butyl nitrate.

[51] Methyl chloride emissions appeared to be emitted by the water column within the rice paddy ecosystem [*Redeker et al.*, 2000, 2002]. Methyl bromide, ethyl chloride, and DMS emissions showed statistically significant positive correlations with methyl chloride ($R = 0.63$, 0.66 and 0.79); however, methyl bromide to methyl chloride correlations have been poor in several previous studies [*Redeker et al.*, 2002]. DMS emissions were sensitive to rice presence, unlike methyl and ethyl chloride emissions, which were the same in planted and unplanted regions of the rice paddy (Figure 3). We suggest that methyl and ethyl chloride emissions were driven by similar processes (algae in the water column), which were separate from DMS and methyl bromide production (rice-plant-mediated).

[52] Methyl bromide, methyl iodide, bromoform, and 1-butene correlated positively with each other (range 0.64 to 0.96) with the exception of the 1-butene/methyl iodide and methyl iodide/bromoform pairs. We have shown that methyl bromide and methyl iodide production were dependent on rice and were not emitted substantially via the water column [*Redeker et al.*, 2000, 2002]. It would be unlikely that 1-butene is not photochemically produced, but these results suggest that future studies of 1-butene production from terrestrial plants may be worthwhile. Bromoform is known to be emitted from several macroalgea [*Carpenter and Liss*, 2000; *Manley and Barbero*, 2001] although emissions by terrestrial plants have not yet been observed. Seasonally integrated bromoform emissions in planted chambers (0.025 ± 0.013 mg m^{-2}) were higher than those from control chambers (0.014 mg m^{-2}), but not significantly so. The source for bromoform from rice paddies remains uncertain but may have been caused either by rice mediated processes or via algae in the water column.

3.6. Ambient Concentrations and Atmospheric Impact

[53] The various compounds released via rice paddy agriculture may have significant regional impacts. Methane released from rice paddies may contribute as much as 20% of the annual global source [*Neue and Sass*, 1994; *Sass et al.*, 1999]. Emitted sulfur compounds may increase the number of cloud condensation nuclei, affecting the hydrological cycle and the irradiance of the region [*Charlson et al.*, 1987]. Recent results implicate released volatile organic iodine compounds in aerosol formation as well [*O'Dowd et al.*, 2002]. Hydrocarbon emissions from rice paddies, including alkanes, alkenes, aromatics, monoterpenes, and isoprene, may react with nitrogen-bearing compounds and increase regional ozone concentrations [*Liu et al.*, 1987; *Ryerson et al.*, 2001]. If nitrogen compounds are not present in sufficient numbers, these compounds will decrease the oxidative capacity of the atmosphere through quenching of hydroxyl radicals [*Jacob and Wofsy*, 1988]. Nitrogen-bearing molecules themselves may be emitted from rice paddies, which can then react with regional sources of volatile organic carbon, including those emitted from rice, to produce regional ozone and smog. Halocarbon emissions from the fields, including methyl chloride, methyl bromide, and methyl iodide, will act to decrease the oxidative capacity of the regional air shed by releasing inorganic halogen radicals which catalytically destroy ozone and

modify HO_x and NO_x ratios [*McFiggans et al.*, 2000; *Vogt et al.*, 1999]. Halogen chemistry is particularly efficient through heterogeneous reactions, with recent research suggesting that halogen radical release is underestimated in most models [*Jacob*, 2000; *Matthew et al.*, 2001].

[54] We observed ambient concentrations ($t = 0$ samples; height $= 1$ m) to be highly variable over the course of the season with at least one incursion of heavily polluted air on 8 June 2000.[1] While difficult to assess, the impact of rice paddy emissions are likely to include an increase in ambient methyl iodide concentrations from 2.1 to 36 pmol mol^{-1}, an increase in ambient DMS concentrations from 2 to 40 pmol mol^{-1} and an increase in isoprene from 70 to 360 pmol mol^{-1}. Maximum ambient concentrations for these gases can be found on days of maximum emission for each compound (Figure 3).[1]

[55] The methyl iodide concentrations observed on the dates with the highest ambient concentrations are more than sufficient to produce photochemical catalytic reactions that have been shown to affect HO_x and NO_x cycles in the lower atmosphere. At concentrations equivalent to 10 pmol mol^{-1} (part per trillion by mole, equivalent to a part per trillion by volume for ideal gases) methyl iodide, the denitrification of the lower atmosphere through iodine chemistry is on the same order of magnitude as HO_x chemistry [*Davis et al.*, 1996; *McFiggans et al.*, 2000], while at 6 pmol mol^{-1} ambient methyl iodide concentrations HO_2 concentrations have been shown to decrease by up to 25% [*Alicke et al.*, 1999]. It is also likely that the 500–2000% increases in ambient DMS and isoprene will have some regional effects.

[56] The integrated emission of isoprene from rice paddies would, if extrapolated to global rice areas (1.45×10^{12} m^2), account for 13 Gg (Gg $= 10^9$g) of isoprene annually. This flux is small compared to the combined total of isoprene sources (570 Tg isoprene annually) [*Guenther et al.*, 1995]. DMS emissions were also small compared to the global sulfur cycle. Emissions of DMS, extrapolated globally, annually from rice paddies, are equivalent to 22 Gg yr^{-1} or 0.1% of annual global emissions (24.5 Tg yr^{-1}) [*Watts*, 2000]. Despite their minor role in global cycling of isoprene and DMS, rice paddy emissions may have regional impact, particularly in intensive agricultural regions.

[57] Rice paddies may contribute nearly 4.5% of the methyl iodide in the lower atmosphere, while rice generated methyl bromide may account for 1.8% of tropospheric methyl bromide (Redeker and Cicerone, submitted manuscript, 2003). Methyl chloride from rice paddies does not have a significant effect on the global methyl chloride cycle (< 0.1%) (Redeker and Cicerone, submitted manuscript, 2003). Extrapolated to global rice land coverage we calculate an annual emission of 1 Gg of ethyl chloride. J. C. Low et al. (unpublished data, 2002) and data from the Transport and Atmospheric Chemistry Near the Equator—Pacific archives (available at http://www-gte.larc.nasa.gov/trace/TP_dat.htm, 2002) suggest an average global concentration of 2.6 pmol mol^{-1} and a calculated average turnover time of ~1 month for ethyl chloride. The global burden and the necessary annual source of ethyl chloride to the atmosphere for these values are 25 Gg (1 Gg $= 10^9$g) and 300 Gg yr^{-1}. These estimates suggest that rice paddy agriculture does not contribute significantly to atmospheric ethyl chloride concentrations.

[58] Extrapolated bromoform emissions from rice paddies is 0.04 Gg yr^{-1}, which, as expected, is much smaller than the flux estimated annually for brown algae (135 Gg yr^{-1}). Brown algae accounts for 60% of the annual global flux (220 Gg yr^{-1}) [*Carpenter and Liss*, 2000].

3.7. Biomass Burning

[59] Estimated emissions from burning of rice paddy residues are listed in Table 1. These values are based in part on measurements and in part on estimates from similar crop residues [*Andreae and Merlet*, 2001]. While the *Andreae and Merlet* [2001] study provides information on many chemical species, only data for the species measured within the Houston study are listed in Table 1. Any compound marked "NR" in Table 1 was not reported in the *Andreae and Merlet* [2001] study. The estimates in Table 1 assumed a postharvest dry biomass weight of 750 g m^{-2}. This is a reasonable estimate of average biomass residue weight, consistent with standing biomass measured at the end of this study [*Sass et al.*, 2002].

[60] In general, biomass burning releases orders of magnitude more of each compound within a few days than was emitted over the course of the entire growing season. Exceptions to this rule include several compounds whose emissions are mediated by rice during the season, including methane, isoprene, monoterpenes, methyl bromide, and methyl iodide. Other compounds where emissions were observed over the course of the season and estimates of biomass burning were not provided, but are assumed to be minor due to their highly reduced state, are alkyl nitrates, bromoform, bromodichloromethane, ethyl chloride, and dimethyl sulfide.

4. Conclusions

[61] This study examined emissions of 55 separate chemical species over the majority of the growing season near Houston, Texas to assay atmospheric impact of flooded rice paddy agriculture. Emissions or upper limits of flux for alkanes, alkenes, ethyne, aromatics, CFCs, halons, halocarbons, dimethyl sulphide, and alkyl nitrates were reported. We observe potentially growth-stage-dependent emissions for several compounds including isoprene, DMS, methane, hexane, methyl bromide, and methyl iodide. Compounds that are potentially produced/induced photochemically within the water column include alkenes and alkyl nitrates while compounds that may be biologically generated in the water column include methyl chloride, ethyl chloride, bromoform, bromodichlorocarbon, hexane, and benzene. This study presents data from a particular set of field management practices and will need to be duplicated in many other field conditions for entire growing seasons before an accurate assessment of fluxes from global rice paddies can be obtained. Further research into the effects of temperature, cultivar, diurnal cycles, and field flooding on emissions of these compounds will also be necessary.

[62] In general, alkane, aromatic, and alkyne emissions were not observed during the season; however, there were observable alkene (11 mg m^{-2}) and isoprene (8.9 mg m^{-2}) emissions. Seasonal halocarbon emissions were similar to previously reported values for methyl halides (2.3, 1, and 31 mg m^{-2} for methyl chloride, methyl bromide and methyl

iodide) and the first terrestrial emissions of bromoform ($25 \ \mu g \ m^{-2}$), bromodichlorocarbon ($2.9 \ \mu g \ m^{-2}$), and ethyl chloride ($0.6 \ mg \ m^{-2}$) were reported. CFC and halon uptake was not observed in this study as it has been in previous studies. We report the first terrestrial source of alkyl nitrates ($0.41 \ mg \ m^{-2}$ per season), which may act as a regional source of reactive atmospheric nitrogen. Dimethyl sulfide emissions were observed, with seasonal emissions slightly larger than previously reported values ($15 \ mg \ yr^{-1}$, growing season only).

[63] The emission of methane from rice paddies is recognized as having global atmospheric relevance, and the role of rice paddies in generating globally significant amounts of methyl bromide and methyl iodide has also been recently reported. This study shows ambient concentrations of isoprene, DMS, and methyl iodide over Houston rice paddies of 360, 40, and 36 $pmol \ mol^{-1}$ concurrent with maximum emissions of these compounds from rice paddies. Regional chemistry can be affected by methyl iodide concentrations of this magnitude. It remains to be seen whether regional chemistry is affected significantly by the observed maximum concentrations of isoprene and DMS. The production of alkenes, while not directly observed in ambient air samples, may also influence regional chemistry.

[64] Biomass burning produces orders of magnitude larger emissions of most compounds than emissions from the rice paddy during the growing season. The few compounds where this is not the case include methane, methyl bromide and methyl iodide, isoprene, DMS, alkyl nitrates, bromoform, and bromodichloromethane.

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D. Blake and S. Meinardi, Department of Earth System Science, University of California, Irvine, CA 92697-3100, USA. (drblake@uci.edu)

K. R. Redeker, QUESTOR Centre, Queen's University of Belfast, Belfast BT9 5AG, UK. (k.redeker@qub.ac.uk)

R. Sass, Department of Ecology and Evolutionary Biology, Rice University, Houston, TX 77251, USA. (sass@ruf.rice.edu)