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Environmental controls over methyl halide emissions from rice paddies

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[1] This paper examines primary controlling factors that affect methyl halide emissions from rice paddy ecosystems. Observations of four cultivars under multiple growth conditions during studies in commercial fields and the University of California, Irvine, greenhouse lead to the conclusion that daily emissions of methyl halides are primarily determined by the growth stage of the rice plant, with the exception that methyl chloride emissions show no clear seasonal pattern. Methyl chloride emissions appear to be more from the paddy water and/or soil as opposed to the plants; however, in soils with high chloride content, these emissions appear to peak during the reproductive phase. Strong secondary influences include air temperature, soil halide concentration, and soil pore water saturation. The cultivars studied had statistically separate seasonally integrated emissions. Irradiant light and aboveground biomass appear to have little effect on emissions. Emissions of methyl chloride, methyl bromide, and methyl iodide are estimated to be 3.5, 2.3, and 48 mg/m^2/yr, or 5.3, 3.5, and 72 Gg/yr, from rice paddies globally. *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 1610 Global Change: Atmosphere (0315, 0325); 1615 Global Change: Biogeochemical processes (4805); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; *KEYWORDS:* environmental factors, methyl halides, rice

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1. Introduction

[2] A significant portion of halogen radicals found in the atmosphere is derived from methyl halide gases, which are produced at the surface of the Earth through both natural and anthropogenic processes [*Davis et al.*, 1996; *Khalil*, 1999]. In the stratosphere, 25% of ozone loss is due to catalytic heterogeneous chemical reactions involving Cl and Br atoms released from methyl chloride (MeCl or CH_3Cl) and methyl bromide (MeBr or CH_3Br) [*Weisenstein et al.*, 1992; *Schauffler et al.*, 1993]. In the troposphere, elevated methyl iodide concentrations (MeI or CH_3I) may increase aerosol formation, affecting regional radiative balance and rates of heterogeneous reactions [*O'Dowd et al.*, 2002]. Elevated CH_3I concentrations have also been shown to enhance denitrification and to decrease the oxidative capacity of regional air masses through modification of NO_x, HO_x, and O_x ratios [*Davis et al.*, 1996; *Alicke et al.*, 1999; *McFiggans et al.*, 2000].

[3] Despite their atmospheric importance, methyl halide budgets remain poorly quantified [e.g., *Butler*, 2000]. It is estimated that only 1800 Gg/yr, or 45–50% of the necessary methyl chloride source budget, has been identified. Methyl bromide, the most extensively studied methyl halide, still requires additional sources of 40 Gg/yr to balance the observed sinks, leaving nearly 20% of its annual budget unexplained. More information for both sources and sinks is needed to obtain an accurate estimate of the global methyl iodide budget [*Kurylo and Rodriguez*, 1998].

[4] There are several terrestrial ecosystems that emit methyl halides in globally significant quantities. Indeed, all ecosystems and most plants measured to date have shown some capacity to influence atmospheric methyl chloride, methyl bromide, and methyl iodide concentrations. Previous studies have focused on tropical and temperate plants, parasitic white-rot fungi, shrublands, wetlands, peatlands, salt marshes, and bean, cabbage, rapeseed, and rice agriculture [e.g., *White*, 1982; *Wuosmaa and Hager*, 1990; *Watling and Harper*, 1998; *Varner et al.*, 1999a, 1999b; *Redeker et al.*, 2000; *Rhew et al.*, 2000; *Yokouchi et al.*, 2002].

[5] Accurate global estimates of ecosystem emissions of methyl halides are hampered by lack of knowledge of mechanisms and of extent of variability. Previous studies of terrestrial ecosystems have focused on single parameters, such as aboveground biomass, soil halide content, or diurnal response (the combined effects of light and temperature), and have rarely examined emissions from multiple sites over entire growing seasons/annual cycles. Temporal and spatial variability within rice paddies are addressed by *Redeker et al.* [2002]. This paper presents results from

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Figure 1. The 2001 UCI greenhouse. Bins are filled with Mars, M202, and M103 cultivars. See color version of this figure at back of this issue.

studies in which soil halide content, light and temperature, and cultivar were manipulated to quantitatively explore variability due to each of these parameters. The effect of simulated "rain-fed" field water-management conditions (experimental soils were primarily unsaturated with short periods of complete saturation) on methyl halide emissions from rice is qualitatively described, as well as the emission patterns of methyl halides over the growing season.

2. Experimental Methods

2.1. Study Sites Preparation

[6] The commercial field sites were located in Maxwell, California (39°17′N; 122°07′W), and in Houston, Texas (29°46′N; 96°01′W), and are fully described by *Redeker et al.* [2000, 2002]. Three greenhouse studies were staged in the University of California, Irvine (UCI) greenhouse (33°39′N; 117°51′W) utilizing 12 methyl halide-inert glass bins (Figure 1). Each bin ($0.91 \times 0.91 \times 0.61$ m^3) was made of five glass plates (6.5 mm thickness) bonded with silicon sealant and filled with soil. During the first greenhouse season (1999) the soil used was found to be carbon-poor. Therefore the soils used in the subsequent seasons experiments were obtained from another source, i.e., a freshwater marsh located near the UCI campus. The freshwater marsh soils had an organic carbon content (1.0% organic carbon by weight) similar to that of commercial fields in Houston (0.9%) and Maxwell (~2.0%).

[7] Soil for each experiment was sifted through a 1.27-cm mesh. A cement mixer was used to homogenize the soil and fertilizer. The amount of fertilizer applied was similar to that used on commercial fields, equivalent to approximately 150 lbs N per acre (170 kg N hectare^{-1}), or 15 g N per bin. Fertilizer nitrogen was in the form of ammonium nitrate. The fertilizer used also provided 1.5 g P and 1.5 g S per bin, along with other trace minerals including selenium and manganese. Approximately 750 lbs (340 kg) of soil was sifted and fertilized for each bin. Salt amendments during the 2002 greenhouse experiment were mixed into the soil with the fertilizer; an estimated 500, 15, and 1 mg/kg of sodium chloride, sodium bromide and sodium iodide was added to each amended bin.

[8] Several different cultivars of rice were used throughout these experiments. Varieties M202 and Cocodrie (both *O. sativa japonica* subspecies) were grown in Maxwell and Houston, respectively, during the field experiments. Seasonal aboveground biomass and grain yields for field experiments are reported by *Redeker et al.* [2002]. Cultivars grown in the greenhouse included M103, M202, and Mars (also *O. sativa japonica* subspecies). Greenhouse grain harvest for cultivars M103 and M202 during the second growing season averaged 860 ± 80 g m^{-2}, with no statistical difference between the two. The grain yield for Mars is unavailable as it was harvested before ripening was completed. Aboveground biomass averages for M103, M202 and Mars cultivars ranged from 670 to 940 g m^{-2}, within the range of previously reported biomass and grain yields from commercial fields [*Redeker et al.*, 2002]. Aboveground biomass (straw and grain) yields during the third growing season were between 1250 and 1500 g m^{-2}.

2.2. Chambers and Sampling Procedures

[9] Chamber placements for field studies are described by *Redeker et al.* [2000, 2002]. During the greenhouse experiments, chamber bases were placed in the soil before the rice was planted and were held stable by four PVC rods attached

to a honeycombed circular PVC platform buried at the bottom of the bin. The chamber base was held 7.5–13 cm above the soil-water interface throughout the season. The bottom of the base was kept below the water surface (water depth was >10 cm) in order to maintain a water seal between the base and the water column. A distance of 30 cm between the sampling chamber and the walls of the bin minimized edge effects.

[10] Gas samples were collected in evacuated 0.5-L electropolished stainless steel canisters. The canisters were attached to a stainless steel sampling line connected to the lid of the chamber (chamber volume $\geq$33 L). The sampling line was immersed in an ice bath to keep the samples at a consistently arid humidity. Methyl halide gas concentrations were analyzed within 10 days of sampling on a HP 5890 GC/ECD fitted with a PoraPlot Q column. For further discussion of gas sampling and analysis methods, the reader is referred to *Redeker et al.* [2000, 2002].

2.3. Halide Sample Preparation and Analysis

[11] Soil halides were extracted by shaking 25 grams of soil in 50 mL of distilled deionized (DDI) water for 1 hour. The supernatant was filtered and the extract stored at 4°C. This procedure was repeated 3 times. Plant tissue halides were extracted by boiling 0.5g of plant tissue in 50 mL DDI water and filtering. This procedure was repeated up to 3 times. Soil pore water was collected by syringe from 0.2-cm-diameter stainless steel tubing inserted into the bin soil. Assuming a spherical draw of sample, the pore water collected originated from within 1.5 cm of the sampling port. Plant tissue and soil extracts and soil pore water solutions were measured with ion-selective electrodes using the known addition technique. Further information regarding analyses of halides is given by *Redeker et al.* [2002]. The accuracy of the halide analysis is better than 9% for all halides, with a precision better than 16% for check standards interspersed throughout pore water, soil, and plant tissue extraction samples.

2.4. Ancillary Data

[12] The exterior light levels of the chambers were measured using a combination of a Li-Cor LI190SB Quantum Sensor connected to a CR510X data logger (Campbell Scientific), a Li-Cor 6200, and a spherical radiometer. Interior chamber light levels were observed to be 70% of the measured exterior light levels. During the experiment, light levels were modified using layers of black plastic mesh, which were placed over the chamber. Modification of internal chamber temperatures was accomplished by placing a radiator (attached to an aluminum wrapped copper coil within the chamber and usually acting to cool the chamber) in either an ethanol/dry ice bath or a boiling water bath to cool or warm the chamber, respectively. In this way, internal chamber temperatures ranging between 15° and 45°C were achieved. Temperature and light levels within the chamber were allowed to equilibrate for at least 5 min (temperature) or 15 min (light levels) before samples were taken.

[13] Soil and water temperatures within each bin were not measured as, due their large mass (100 kg water and 340 kg soil), they were expected to reflect the relatively consistent greenhouse temperatures (between 19° and 23°C at night and from 25° to 31°C during the daytime) and to change little over the course of any given experiment (generally <10 min). Seasonal temperatures and relative humidity were tracked during the second growing season using a Campbell Scientific 510 data logger recording data from an HPMC 4950 probe. Relative humidity negatively correlated with temperature and ranged from 60 to 100%.

2.5. Experimental Conditions During Greenhouse Studies

[14] Experiments were conducted over three growing seasons. In the first growing season (1999), three replicates of two separate cultivars and a control were studied. Owing to problems with experimental set-up, only data from temperature and light experiments performed in one bin over a single day and the qualitative pattern of emissions over the course of the season are included in our analysis.

[15] In the second growing season (2001), four replicates of three different cultivars (M103, M202, and Mars) were examined. The cultivars were placed in a diagonal box pattern, four rows by three columns to minimize cultivar-dependent wall and edge effects. An experiment comparing water-management practices was performed by subjecting three replicates of each cultivar to irrigated (continuously flooded) conditions and periodically watering a single replicate of each cultivar to mimic rain-fed water supply. The water supply to the greenhouse during the 2001 experiment was contaminated with excessive levels of halides (0.3–3.0 mM Cl-, 5–25 μM Br-, 0.1 μM I-). The bins were replenished with the contaminated water supply on a weekly basis to replace water lost through evapotranspiration, and were therefore not closed systems for halides. Data reported from these experiments include seasonal emission profiles and the effects of changing temperature and light levels, rice cultivar, water-management, and soil halide concentrations.

[16] In the third growing season (2002), multiple filters were added to the greenhouse water line, and tap water samples were consistently measured to ensure a low background concentration of water halides as well. Pond liners were added to the glass bins to avoid bin fracturing and ensure a closed system where plant and water column emissions would be the only escape route for halide ions. Triplicate analyses of rice grown in soil with and without salt amendments allowed quantification of the effect of soil halide concentrations on methyl halide emission rates.

[17] The potential effects of leaching from the bin liner were studied by placing swatches of bin liner in deionized (DI) water and rocking for 3 days, then analyzing the water using ion-selective electrodes. Ion leaching from the bin liners during this growing season increased soil halide concentrations in all bins. The effect of this leaching on soil chloride and bromide concentrations was small compared to the amounts of these ions added, but iodide concentrations were influenced as much or more by the leachate (>2 mg/kg soil) as by the potassium iodide that was added to the bins. The discussions on light and temperature

and the effects of increased soil halide concentrations incorporate data from this greenhouse experiment.

3. Results and Discussion

3.1. Growth Stage

[18] Results from all studies for methyl chloride, methyl bromide and methyl iodide are shown in Figures 2, 3, and 4. These studies include periods where emissions of methyl halides appeared to be negative, indicating that consumption by the plant or water column within the chamber exceeded production.

[19] Each methyl halide shows consistent seasonal emission rates and profiles under several different environmental conditions (Figures 2–4, Table 1) that are markedly different from the other methyl halides studied. Growth stage appears to set the relative rate of emission of methyl bromide and methyl iodide (Figure 5).

[20] For a complete description of rice growth stages, the reader is referred to International Rice Research Institute (IRRI) journals or our previous papers [*Redeker et al.*, 2000, 2002]. A brief review for clarity is included here.

[21] Rice proceeds through two main growth stages, the vegetative and the reproductive phases (stage = phase). During the vegetative stage the plant expends its energy in height gain and tiller (shoot) generation. The period of maximum growth, in tillers and in height, is called maximum tillering. Maximum tillering generally occurs after 50% of the season has passed, with a possible range of 36 to 62% [*Rice Information cooperative Effort* (*RICE*), 1967]. The plant reproductive period, during which the plant expends its energy primarily in developing grain resources, begins at the end of the vegetative stage and lasts until harvest. Panicle initiation marks the beginning of the reproductive cycle. Panicle initiation occurs concurrently with or up to 2 weeks following maximum tillering. At initiation the panicle is a small translucent structure growing within the stem on which the seeds will grow and develop. It eventually grows through the stem and exits (heading), after which flowers develop and are fertilized (flowering). After flowering the plant devotes its energy to developing the grain (ripening).

[22] For the purposes of this paper the reproductive stage is defined as lasting from panicle initiation until just after flowering. The ripening phase is defined as the remainder of the season after flowering. Heading and flowering, which happen during the reproductive phase, generally occur after 60% (heading) and 70% (flowering) of the entire season has passed. The season is 100% complete at the point of harvest.

[23] The seasonal emission patterns of methyl halides are shown in Figure 5. Each methyl halide shows a separate and distinct pattern (the lack of seasonality associated with methyl chloride may be considered a pattern of sorts). Methyl iodide emissions peak early in the season, before maximum tillering. Leaf methyl iodide emission potential (defined as g MeI g FW^{-1} day^{-1} from a leaf disk in a 0.1-M solution of sodium iodide) decreases sharply during the first few months of rice growth [*Redeker et al.*, 2003]. Maximum methyl iodide emissions appear to occur when the product of leaf emission potential and leaf biomass is highest. The data from rice under continuously flooded conditions show that maximum emissions occur between 30 and 35% of the season duration. A smaller, secondary maximum of methyl iodide emissions occurs near the flowering stage, or between 60 and 80% of the season duration (Figure 4). This small increase in methyl iodide emissions was statistically different for the Mars and Cocodrie cultivars during the Houston, Texas, 2000 and UCI greenhouse, 2001 studies; however, the increase observed during flowering was not significant for cultivars M103 and M202 during either the 1998 and 1999 Maxwell, California, studies (approximately days 80 and 100) or the 2001 and 2002 UCI greenhouse studies (approximately day 90 for both) (Figure 4) [*Redeker et al.*, 2002].

[24] Maximum methyl iodide emissions are delayed in rice fields that have been drained and re-flooded or were flooded at a later seasonal period. The explanation for this may be connected to the production of leaf-tissue biomass. In fields that are delayed in flooding or are drained and re-flooded the increase in plant biomass is slowed [*Redeker et al.*, 2002]. A decrease in the rate of leaf-tissue generation diminishes the product of leaf emissions potential and biomass, delaying the maximum peak and decreasing the maximum daily flux.

[25] In contrast to methyl iodide, maximum emissions of methyl bromide occur during the latter half of the season. Maximum methyl bromide emissions occurred after 60% of the season had passed. Methyl bromide emissions appear to reach seasonal maxima after heading, then fluctuate on weekly timescales (Figure 3). MeBr leaf emission potentials remain constant during the period when emissions attain their maxima, which may explain why methyl bromide seasonal emissions are relatively unaffected by field flooding date [*Redeker et al.*, 2003].

[26] Methyl chloride emissions do not appear to depend on the growth stage of the rice plant, with maximum and near maximum emissions occurring throughout the season (Figures 2 and 5). The slight elevation in emissions seen in the running mean (Figure 5) is not statistically significant. Control chamber fluxes of methyl chloride are nearly equivalent to planted chamber fluxes (Table 1, Figure 2). This result, combined with high variability, lack of seasonality, and general insensitivity to changes in air temperature

Figure 2. Averaged methyl chloride emissions data from all studies. Open and solid black squares represent M202 cultivar studies. Open squares represent differing conditions of growth: during the 1998 and 1999 Maxwell seasons open squares indicate rice results from Burnt Straw fields, while in the 2002 greenhouse, they represent rice grown in soil amended with salt. Red triangles indicate unplanted control plots in all studies. Dark blue open circles represent the cultivar Cocodrie and solid blue circles represent the Mars cultivar. Dark purple diamonds represent M103, a commonly grown cultivar in California. Figures 2a and 2d have two replicates per data point, while Figures 2b, 2c, 2e, and 2f have triplicate analyses. All graphs are at the same scale except Figure 2f. Error bars represent 1 standard deviation. See color version of this figure at back of this issue.

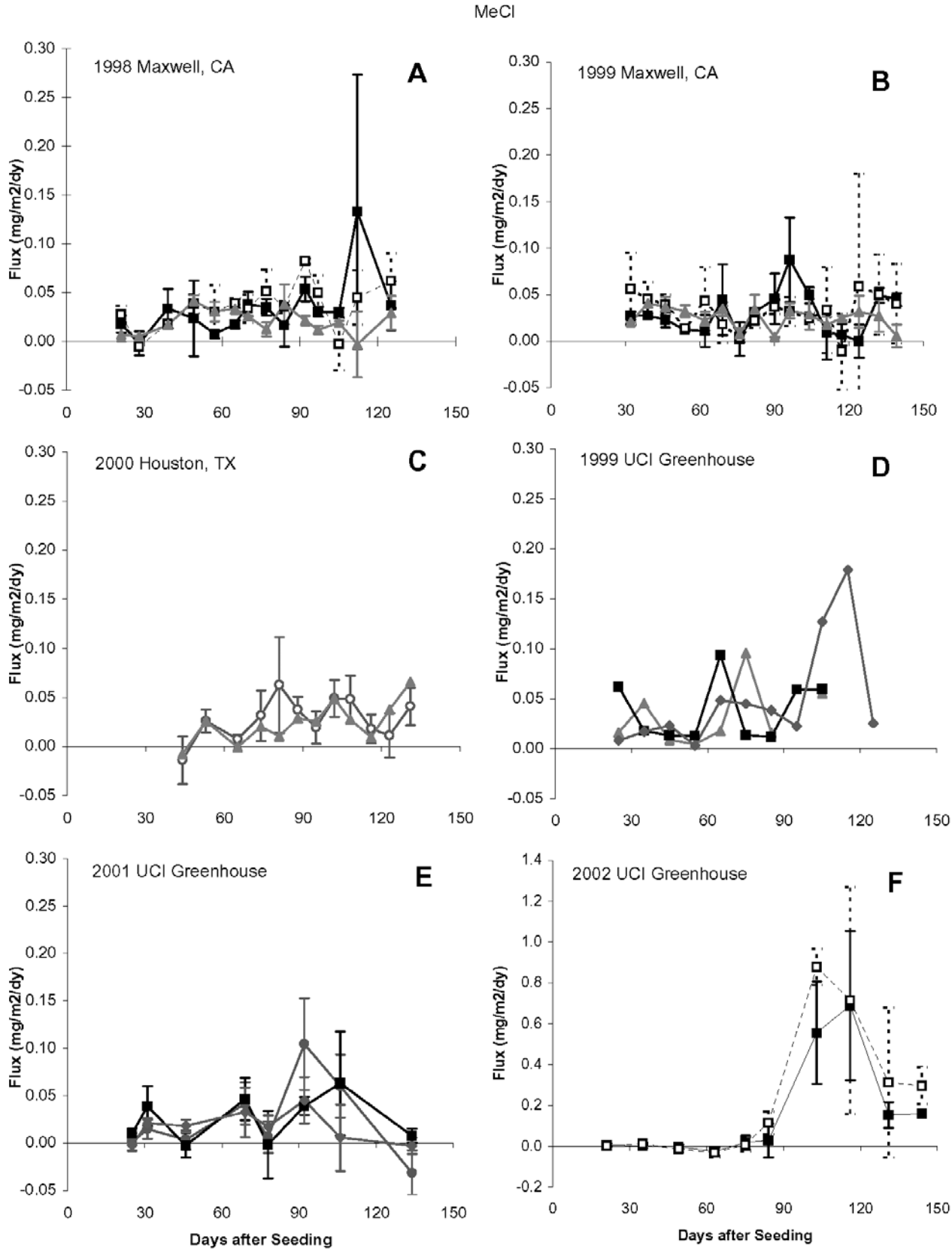
MeCl
1998 Maxwell, CA
A
1999 Maxwell, CA
B
2000 Houston, TX
C
1999 UCI Greenhouse
D
2001 UCI Greenhouse
E
2002 UCI Greenhouse
F
Flux (mg/m2/dy)
Days after Seeding

Figure 2.

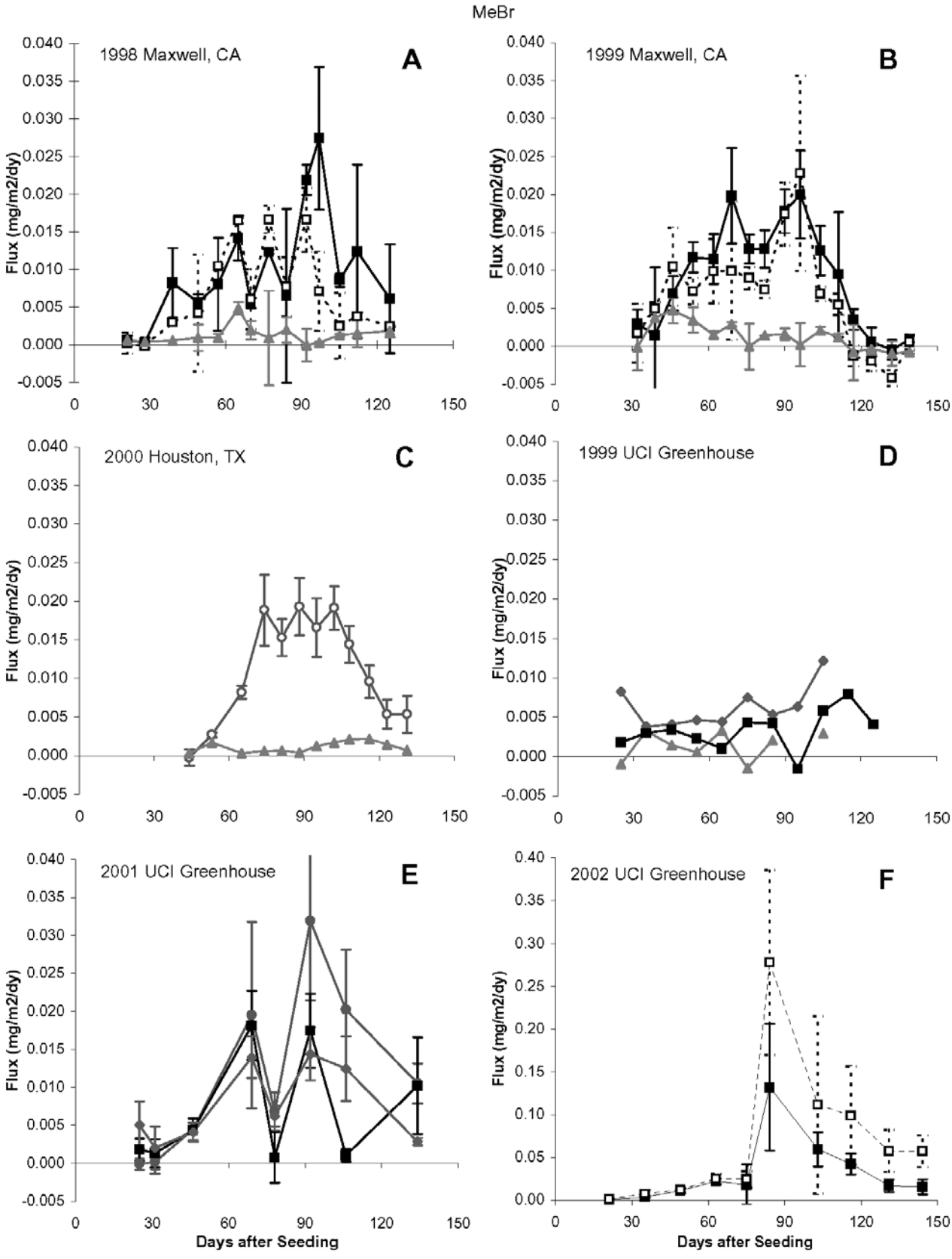

Figure 3. Results for methyl bromide as described for Figure 2. See color version of this figure at back of this issue.

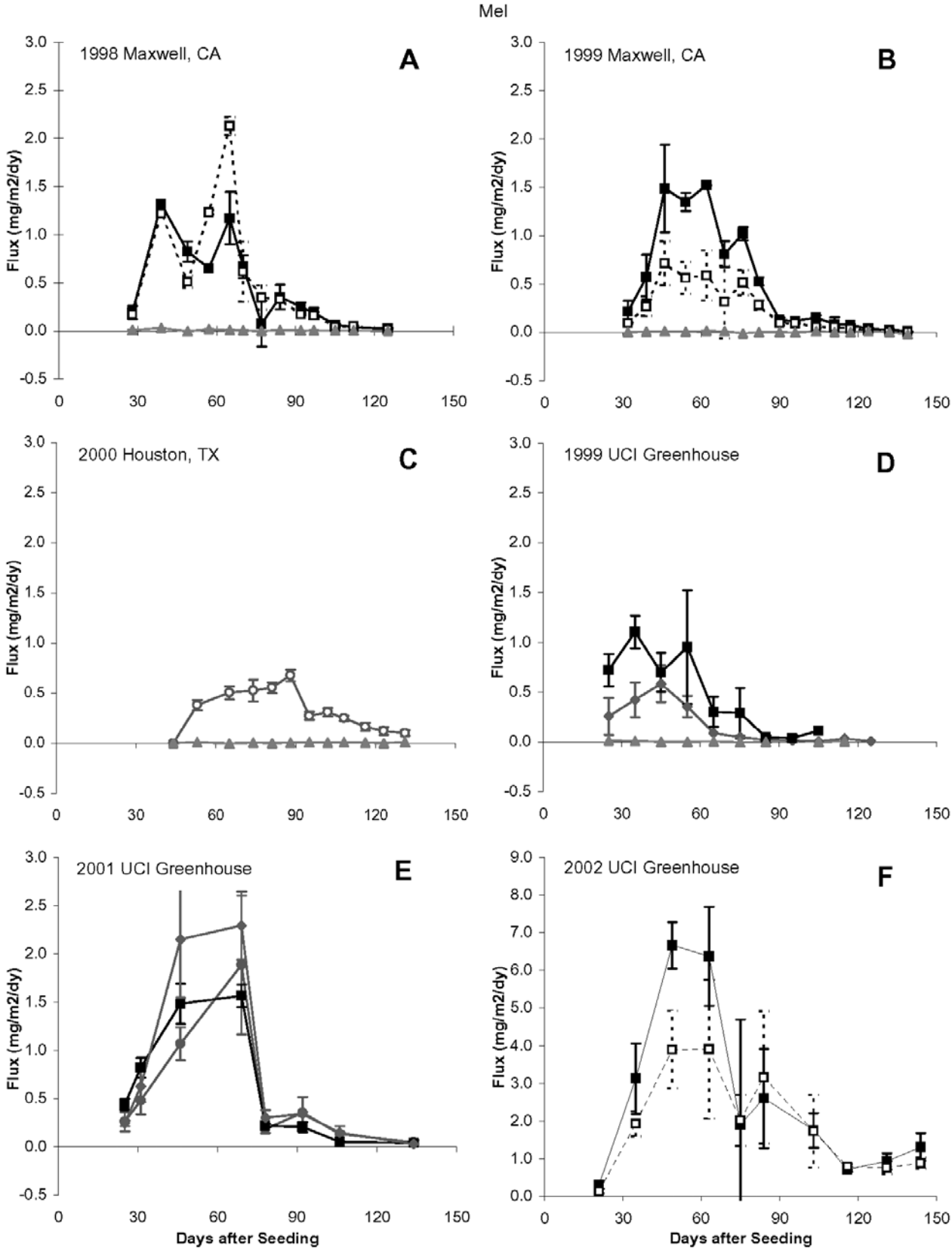

Figure 4. Results for methyl iodide as described for Figure 2. See color version of this figure at back of this issue.

Table 1. Seasonally Integrated Emissions of Methyl Halides From All Studies[a]

	Commercial Field Studies			UCI Greenhouse Studies		
	MeCl	MeBr	MeI	MeCl	MeBr	MeI
			1998			
			Maxwell, California			
Straw Inc.	4.1 (3.0)	1.1 (0.5)	48.8 (8.4)			
Burnt straw	4.2 (1.7)	0.7 (0.2)	56.2 (4.6)			
Control	2.6 (1.1)	0.1 (0.1)	0.7 (0.4)			
			1999			
			Maxwell, California			
Straw inc.	3.7 (1.7)	1.1 (0.4)	62.0 (11.7)			
Burnt straw	3.9 (3.3)	0.8 (0.4)	28.1 (10.1)			
Control	3.0 (0.9)	0.2 (0.2)	0.5 (0.9)			
			Preliminary study			
M103				5.4	0.4	20
M202				4.5	0.8	49
Control				3.6	0.1	0.4
			2000			
			Houston, Texas			
Cocodrie	2.3 (2.3)	1.0 (0.2)	30.8 (4.4)			
Control	2.1	0.1	0.3			
			2001			
			Cultivar differences			
Mars				2.5 (4.5)	1.1 (0.7)	52.3 (30.5)
M202				2.2 (3.7)	0.7 (0.6)	64.8 (32.4)
M103				1.1 (2.8)	0.9 (0.5)	78.4 (38.0)
			2002			
			Soil halide effects			
M202				22.2 (12.6)	4.2 (2.2)	342 (102)
M202 + halide				31.8 (18.8)	7.6 (4.2)	256 (96)

[a]Trapezoidal integration was used to calculate seasonal emissions, assuming zero emissions at day 0 and harvest. Emission rates are given in mg/yr. Standard deviations of results are listed in parentheses. Commercial fields in Maxwell, California, used the cultivar M202 straw treatments where either the straw was re-incorporated into the fields or was burned off at the end of the previous season. Greenhouse experiments during 2001 and 2002 are corrected for temperature and are listed at seasonal emissions expected for 30°C.

and irradiant light, suggests that most or all methyl chloride is generated in the water column. The possibility that methyl chloride is produced by processes in the soil beneath the water column cannot be dismissed. Like methyl bromide, methyl chloride emissions appear to be relatively unaffected once field flooding occurs.

[27] There is a possibility that increased soil chloride content may elevate methyl chloride emissions from rice plants above the rice paddy background (Figure 2f). If this occurs, then maximum methyl chloride emissions occur during the reproductive and ripening phases (between 60 and 80%). However, unplanted paddy emissions under elevated soil halide concentrations were not measured so this hypothesis remains unconfirmed.

3.2. Diurnal Response (Light and Temperature)

[28] Diurnal patterns in methyl halide emissions have been reported from various ecosystems, including peatlands, rice paddies, bean plants, shrublands, and salt marshes [*Amiro and Johnston*, 1989; *Muramatsu and Yoshida*, 1995; *Rhew et al.*, 2000, 2001, 2002; *Dimmer et al.*, 2001]. In all cases, methyl halide emissions increase concurrently with active radiation and are at their minimum at night. These studies note diurnal response but do not separately quantify the effects of light and temperature.

[29] The effects of light and temperature were studied during each of the three greenhouse growing seasons. A subset of the temperature and light studies were diurnal studies, where emissions were measured between midnight and three in the morning and compared to data from the previous day (samples taken between 1000 and 1400 local time). Generally, a quantifiable light or temperature response for methyl chloride is not seen. Methyl bromide and methyl iodide however, show specific temperature responses that depend on cultivar and that change over the course of the season (Table 2).

Figure 5. Emissions versus growth stage of the rice plant. The *x* axis represents the relative amount of the season from planting to harvest that has passed. The *y* axis represents relative emissions as determined by assigning the maximum emissions during each season a relative flux of 100%, while relative emissions for all other emissions are calculated by dividing by the seasonal maximum flux. Average daily results for methyl chloride, methyl bromide, and methyl iodide are shown. Methyl chloride and methyl bromide graphs include all seasons data, while results for methyl iodide only include continuously flooded field results (1999 Maxwell, 1999 Greenhouse, 2001 Greenhouse, 2002 Greenhouse). The lines in each figure are smoothed point-to-point fits for fluxes averaged in 5-day bins.

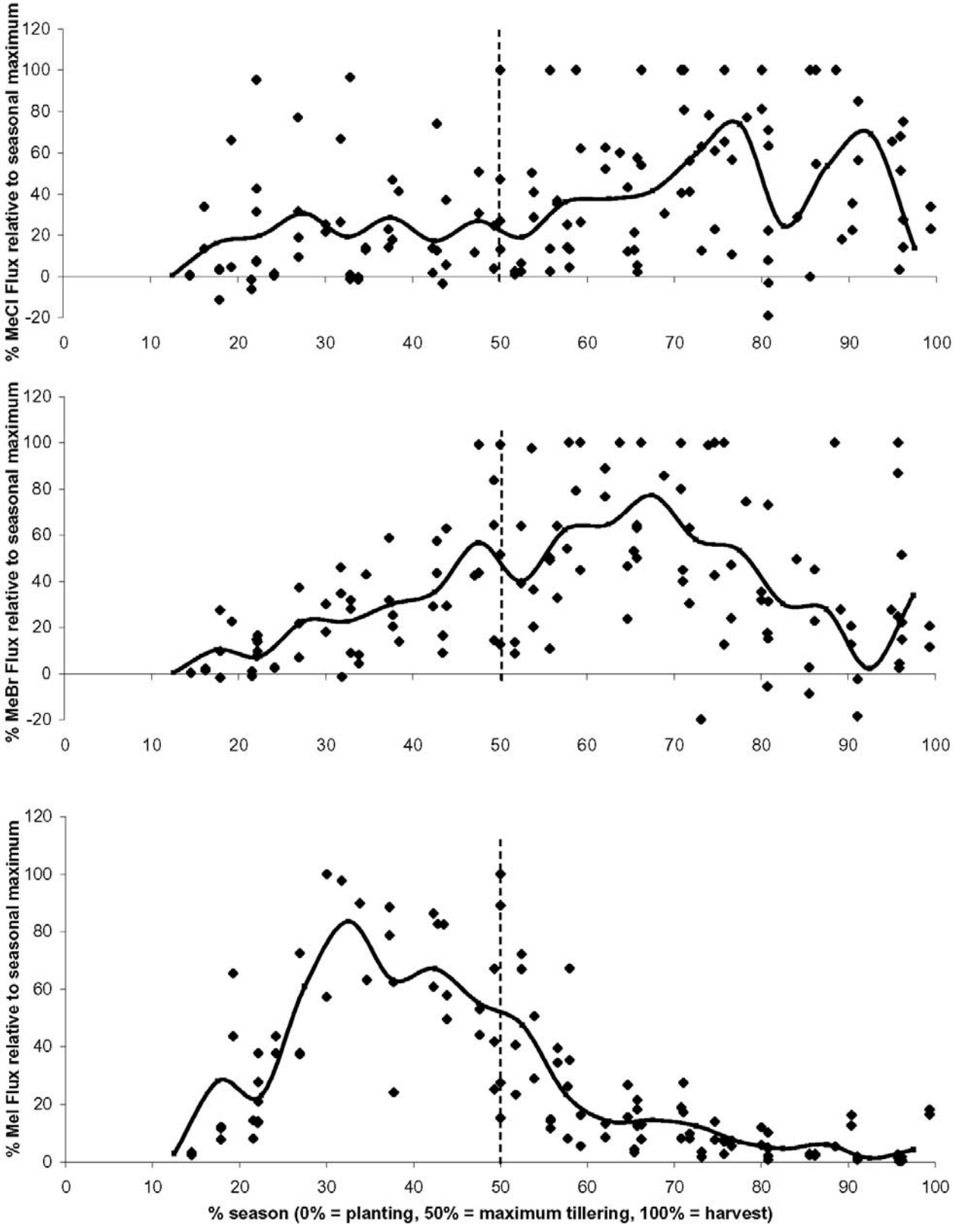
% MeCl Flux relative to seasonal maximum
% MeBr Flux relative to seasonal maximum
% MeI Flux relative to seasonal maximum
% season (0% = planting, 50% = maximum tillering, 100% = harvest)

Figure 5.

Table 2. Least Squares Regressions for Cultivar-Dependent Temperature Response During Tillering, Reproductive, and Ripening Stages[a]

	Tillering		Reproductive			Ripening	
	MeBr	MeI	MeCl	MeBr	MeI	MeBr	MeI
				1999, M103			
m						**0.053**	0.072
b						**−0.593**	−1.163
σ_m						**0.032**	0.009
σ_b						**0.775**	0.216
R^2						**0.16**	0.77
				2001, Mars			
m	**0.198**	0.061				**−0.022**	0.098
b	**−4.524**	−0.817				**0.888**	−1.538
σ_m	**0.033**	0.005				**0.029**	0.017
σ_b	**0.951**	0.141				**0.826**	0.359
R^2	**0.84**	0.96				**0.04**	0.69
				2002, M202			
m	**0.096**	0.044	*0.131*	**0.067**	0.069	**0.021**	−0.002
b	**−1.888**	−0.357	*−2.938*	**−1.084**	−1.069	**0.373**	1.054
σ_m	**0.057**	0.011	*0.023*	**0.013**	0.005	**0.040**	0.017
σ_b	**1.575**	0.362	*0.728*	**0.345**	0.128	**1.260**	0.528
R^2	**0.26**	0.56	*0.77*	**0.83**	0.97	**0.04**	0.00

[a]For data that go through an inflection point, only the data below the temperature cut-off are used for the linear regression. Results may be applied using the linear approximation $y = m \times x + b$ with σ_m and σ_b equivalent to the standard deviation of the slope and y-intercept, respectively. Units for all tabulated values are "increase in emissions relative to 30°C (IER)/°C." All data pertaining to MeBr are bold; all data pertaining to MeI are italic.

3.2.1. Effects of Temperature

[30] The studies on the effects of temperature examined three cultivars of rice during the tillering, reproductive, and ripening growth stages. The results of these observations are listed in Table 2. Temperature responses of rice plant emissions of methyl bromide and methyl iodide are shown in more detail in Figures 6 and 7.

[31] As in Figures 2–4, there are some negative fluxes shown in Figure 6. This shows that consumption of methyl bromide by the water column and/or the rice is greater than the emission of methyl bromide by the rice plant during these measurements. If we assume that the water column is consuming methyl bromide at a relatively constant rate, then this suggests that either the rice plant is producing less methyl bromide at colder temperatures or that the rice plant has shifted from a production to a consumption mechanism due to the colder temperatures.

[32] It was observed that temperature has a strong effect on methyl bromide and methyl iodide emissions, as *Muramatsu and Yoshida* [1995] found for methyl iodide. Methyl chloride emissions are generally insensitive to ambient temperatures within the sampling chamber. However, a strong correlation between methyl chloride emissions and temperature was observed for the M202 cultivar during the reproductive stage of the third growing season. This solitary result supports the hypothesis that sufficiently elevated soil chloride concentrations can cause the rice plant to emit enough methyl chloride to override the water column emissions that generally dominate rice paddy fluxes (see sections on soil halide concentrations and growth stage). Likewise, this single observation of dependence on temperature may indicate that methyl chloride emissions, when produced by the rice plant, occur mainly during the reproductive period.

[33] Figure 6 shows methyl bromide emissions relative to 30°C emissions. The 30°C emissions value was calculated from linear regressions of observed emissions versus temperature from a single day of diurnal testing. The data shown in Figures 6 and 7 were adjusted via the ratio of the observed emissions to the calculated 30°C value; i.e., if the value for emissions of methyl bromide at 30°C was calculated to be 20 $\mu g/m^2$/day, and a set of samples at 20°C were measured with a flux of 10 $\mu g/m^2$/day, then the data on Figure 6 would be set at 20°C and 50% emissions relative to 30°C.

[34] Methyl bromide emissions and their dependence on temperature are easily separable into two time periods, from tillering through reproductive stages and the ripening stage. The tillering and reproductive periods show strong temperature dependence, but, as the plant senesced during the ripening stage, no quantifiable relationship between emissions and temperature was observed (Figure 6). It is posited that the rice plant, during senescence, was less capable of regulating enzymatic processes and that competing methyl transferase reactions within the leaf tissue created the random pattern that was observed [*Redeker et al.*, 2003]. During the early stages of rice growth, M202 and Mars cultivars maintained a positive correlation between methyl bromide emissions and temperature. M202 temperature dependence has an inflection point near 36°C, while the temperature dependence for the Mars cultivar remains linear beyond 36°C (Table 2, Figure 6). M202 response to temperature is statistically similar through the tillering and reproductive stages. Despite positive temperature dependences of the same order of magnitude, the slopes of the temperature response between cultivars are significantly different, with Mars showing a much greater response to temperature changes, 0.198 ± 0.033, than M202, 0.096 ± 0.057 (IER) (increase in emissions relative to 30°C)/°C (Table 2).

[35] Methyl iodide emissions and their dependence on temperature also separate into two growth periods, although for methyl iodide these observations fall into tillering versus reproductive and ripening stages (Figure 7). The main difference between the two groups is the appearance of a temperature-dependent emissions maximum between 30 and 38°C during the later season, and a slight increase in the temperature response of the plants. The Mars cultivar had a statistically higher response to temperature than the M202 cultivar during tillering; slopes for each are 0.061 ± 0.005 and 0.044 ± 0.011 IER/°C (Table 2). These slopes correspond to an increase of 190 and 160% in methyl iodide emissions over a ten-degree (25–35°C) temperature range. During the reproductive and ripening stages, emissions of methyl iodide appear to peak between 30 and 38°C. Below this inflection point, all cultivars exhibit statistically significant elevated responses to temperature, with slopes equivalent to 0.098 ± 0.017, 0.069 ± 0.005, and 0.072 ± 0.009 IER/°C for Mars, M202, and M103. These results are in agreement with *Muramatsu and Yoshida* [1995], who reported a diurnal increase of approximately 2 times more

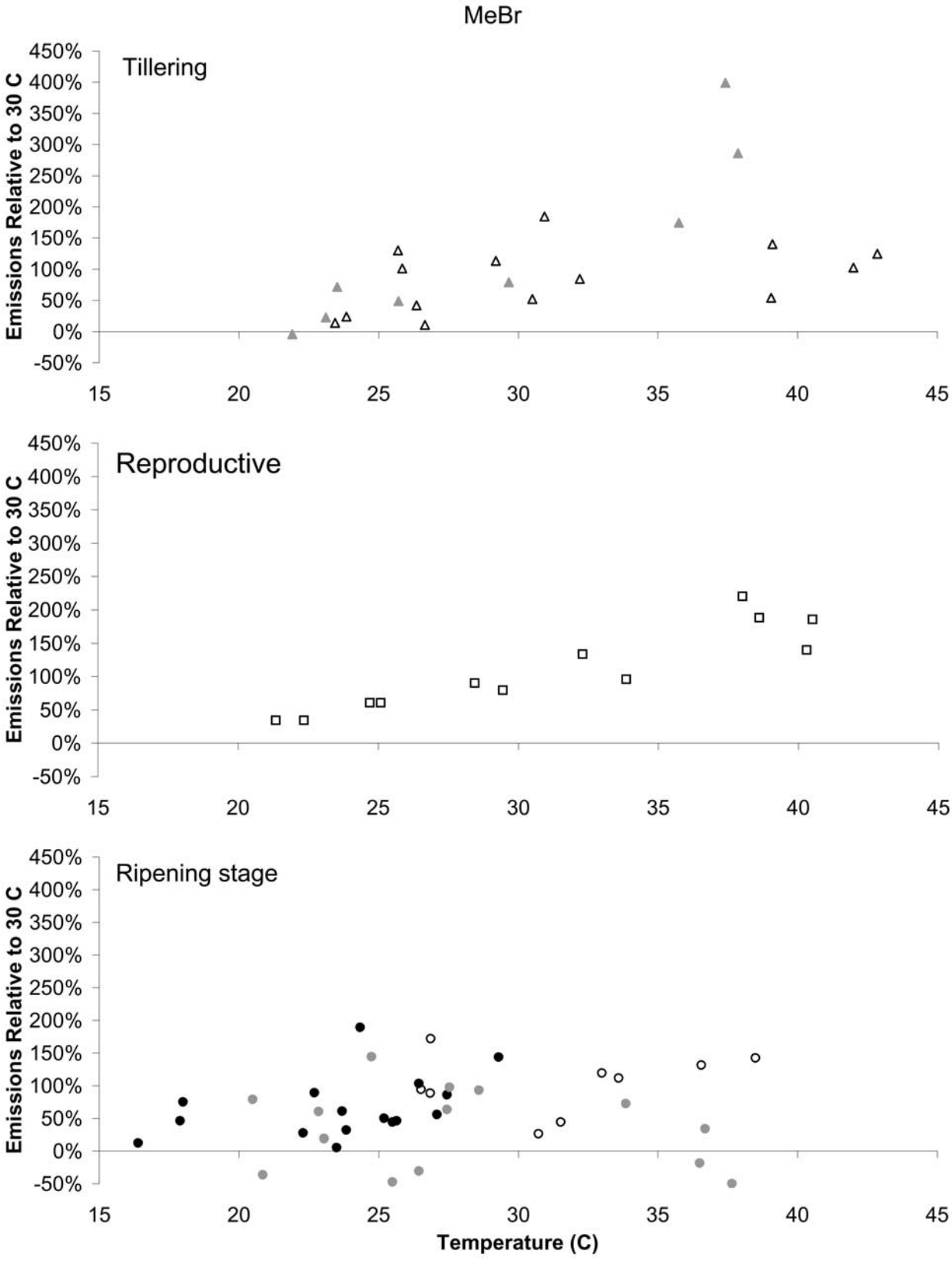

Figure 6. Comparison of the effect of temperature on methyl bromide emissions at different growth stages. Data from three different experiments are shown, with cultivars studied identified as: M202, open black; M103, solid black; Mars, solid shaded. The studied growth stage is identified by shape of symbol: triangles, tillering; squares, reproductive; circles, ripening.

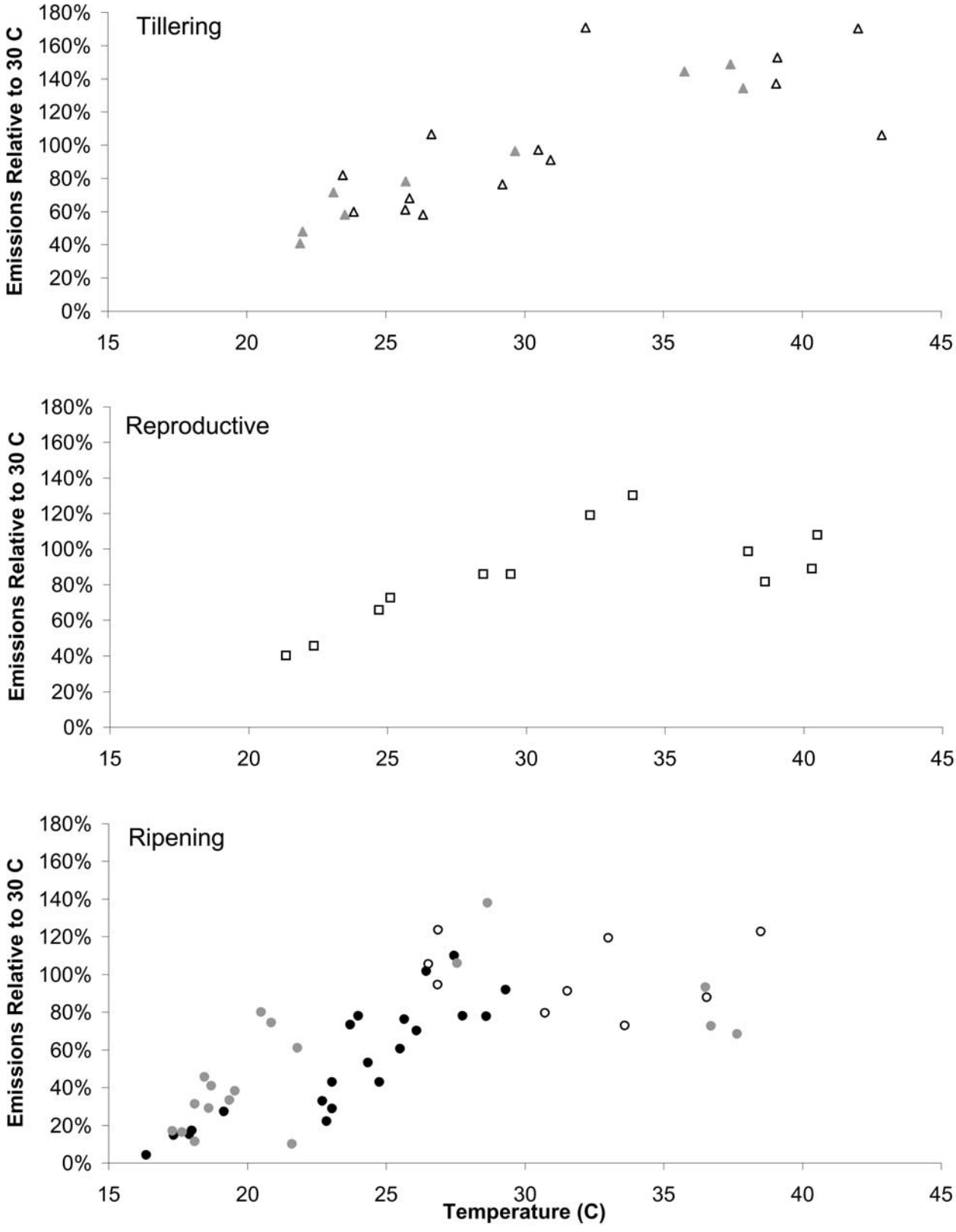

Figure 7. Comparison of the effect of temperature on methyl iodide emissions at different growth stages. Symbols denote the same cultivar and growth stage as defined in Figure 6.

emissions of methyl iodide from the Nipponbare cultivar, during the ripening stage, with a temperature differential of 7° between day and night.

[36] It should be noted that over a 10° temperature range, from 25 to 35°C, these results suggest that methyl bromide emissions will increase by up to 6 times for the Mars cultivar and will double for M202. Methyl iodide emissions over the same temperature range will increase by a factor of 2 for all cultivars. These results may explain the peatland diurnal response described by *Dimmer et al.* [2001], which was reported based on increased fluxes of methyl bromide and methyl iodide during the daytime. The peatland chamber temperatures increased by as much as 15°C over a sampling period of 30 min. In contrast, the sampling procedures used during the temperature experiments performed in the UCI greenhouse allowed the plants to equilibrate for up to 10 min, then the plants were enclosed and sampled at 5, 9, and 13 min with chamber temperatures remaining relatively constant over the time period.

3.2.2. Arrhenius Plots and Calculation of Energy of Activation

[37] We have demonstrated the degree to which the data fit a linear form with temperature (Table 2). We also examined whether the data fit an exponential regression (Arrhenius plot, data not shown). Particularly, methyl iodide response to temperature below 35°C over the course of the season showed a reasonable exponential fit (r^2 ranged from 0.49 to 0.96). A ''net'' activation energy for methyl iodide production in rice plants can be calculated from the slope of the line in an Arrhenius plot. The calculated "net" activation energy ranged from 3.1 kCal/mol for the M202 cultivar during tillering to 15.5 kCal/mol for the M103 cultivar during ripening, with values for the Mars cultivar falling between those of cultivars M103 and M202.

3.2.3. Effects of Light

[38] The maximum effect of irradiance (full sunlight to nighttime levels of irradiance) is calculated to be 10% of the observed temperature dependence. During each study, both the temperature and the light levels were measured along with methyl halide fluxes. The effects of temperature were removed by determining the flux of each methyl halide at 30°C via linear regression of the daytime temperature data (see section 3.2.1). The emissions data normalized to 30°C were plotted against the irradiant light levels measured during the study. The resulting plots show no statistically significant slope from darkness to full daytime sunlight (results not shown). Two daytime studies performed with increased shading and two nighttime studies (between 2300 and 0500 local time) indicate that full sunlight daytime versus shaded daytime versus nighttime fluxes of methyl bromide are statistically identical, as are those of methyl iodide, when normalized to the same temperature (data not shown).

[39] To obtain accurate estimates of global emissions from other ecosystems will require determinations of the temperature dependences of their emissions. On a related note, by these estimates (and assuming plants will not adjust to higher temperatures), methyl bromide emissions from rice plants may be expected to increase by as much as 10 to 45% for a global 1°C temperature increase (from 25° to 26° C), while methyl iodide emissions should increase by 5 to 12%. If other plants exhibit similar temperature dependences, then they, as a response to climate change, may explain some of the twentieth century increase in atmospheric methyl bromide [*Sturges et al.*, 2001].

3.3. Soil Halide Concentration

[40] The majority of soil halide uptake by plant tissue occurs in the first 2 months of growth, with early leaf tissue concentrations of chlorine, bromine and iodine reaching values as high as 34,000, 600, and 50 ppm, respectively, in soils with sodium chloride, sodium bromide and sodium iodide amendments [*Redeker et al.*, 2003; K. R. Redeker et al., unpublished data, 2002]. After initial uptake, plant-tissue halogens are transported to growing biomass, so that by 3 months after planting (the end of the reproductive phase), leaf-tissue halide concentrations have been diluted to 15,000, 500, and 4.5 ppm independent of soil halide concentrations. Rice plant tissue halide concentrations appear to be regulated throughout the growing season [*Redeker et al.*, 2003; K. R. Redeker et al., unpublished data].

[41] The influence of soil halide concentrations on emissions cannot be identified as definitely linear for any of methyl halides due to the large variability associated with both emissions and soil halide concentrations. A comparison of M202 cultivar data from the 1999 Maxwell, California, field experiments and the 2001 and 2002 greenhouse experiments is shown in Figure 8.

[42] Only early season (averaged data from 19 April 2002 and 7 June 2002) soil halide concentrations for the top 10 cm of soil are used for comparison, as they are the most likely to describe root conditions during the phase of growth when soil halide uptake by rice occurs. Table 3 shows soil halide concentration data during the 2002 greenhouse experiment for 0–10 and 10–20 cm depths during tillering, reproductive, and ripening stages as well as a pore water concentration gradient taken just prior to harvest. Soil heterogeneity led to non-uniform distributions of halides in the early season after the initial pulse of water was added to the bins (Table 3). Also, measured leach rates of iodide from the bin liners (while small) added significant amounts of iodide to the system (K. R. Redeker et al., unpublished data).

[43] Early season values of soil halides were influenced by the initial flooding of the bins. Evidently, soil halides were washed to the bottom few centimeters of the bin and diffused upward throughout the season, which explains why the surface soil bromide and iodide concentrations increased over time.

[44] Methyl chloride emissions are positively affected by soil chloride concentration. However, high MeCl emission variability (±70%) makes it difficult to determine if methyl chloride emissions are linear with soil chloride (Figure 8). A linear fit to the data (seasonal integrated emissions (SIE) in mg/m^2, SIE = 0.213 × [Cl-, ppm] - 6.512; R^2 = 0.81) suggests that emissions of methyl chloride will increase by 0.21 mg/yr for every part-per-million increase in soil chloride, although rice grown in chloride-poor soils (<30 ppm) would then be projected to consume methyl chloride. Alternatively, emissions may follow a stepwise

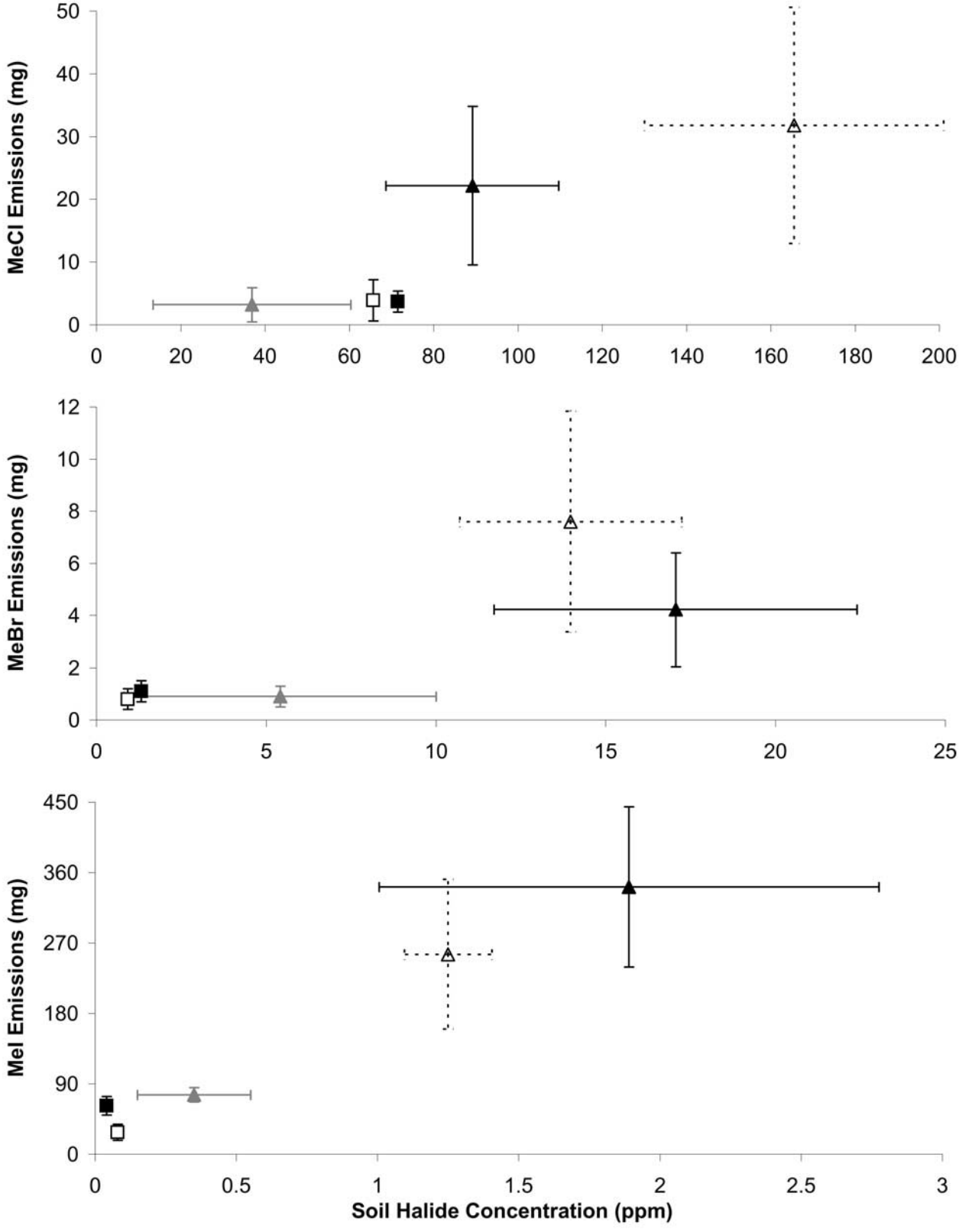
MeCl Emissions (mg)
0
10
20
30
40
50
0
20
40
60
80
100
120
140
160
180
200
MeBr Emissions (mg)
0
2
4
6
8
10
12
0
5
10
15
20
25
MeI Emissions (mg)
0
90
180
270
360
450
0
0.5
1
1.5
2
2.5
3
Soil Halide Concentration (ppm)

Figure 8.

Table 3. Average Soil Halide Concentrations (mg/kg) and Pore Water Halide Concentrations (mM) for the 2002 UCI Greenhouse Study[a]

		M202			M202 + X		
	Depth, cm	Cl	Br	I	Cl	Br	I
Soil Halide Concentrations							
19 April 2002	0–10	89	16.3	1.88	151	8.0	0.87
	10–20	127	6.7	1.46	987	24.0	1.10
7 June 2002	0–10	41	17.8	1.90	180	19.9	1.63
	10–20	154	20.4	2.89	1040	45.5	4.05
24 July 2002	0–10	57	21.0	1.69	299	27.7	1.83
	10–20	144	30.9	3.96	988	56.3	4.40
Pore Water Halide Concentration Depth Profile							
6 August 2002	3	2.68	0.32	0.031	21.80	0.90	0.035
	8	5.62	0.71	0.058	36.60	1.20	0.051
	13	8.79	0.84	0.083	59.73	1.92	0.084
	18	9.11	0.90	0.092	88.97	2.31	0.092
	23	11.60	1.01	0.110	145.33	3.20	0.110
	27	12.57	1.01	0.192	144.00	3.21	0.160
	28	15.17	0.93	0.108	117.47	3.14	0.168

[a]M202 indicates the bins that were not amended with salts while M202 + X indicates bins that were amended. Depths are measured downward from the surface, with 0 cm marking the soil water interface.

pattern where methyl chloride emissions remain constant for soil chloride concentrations below 70 ppm while higher concentrations establish a new equilibrium emission rate.

[45] Methyl bromide emissions are also positively affected by increased soil bromide concentrations. A linear fit of the methyl bromide data is moderately consistent with the data (R^2 = 0.69) and cannot be ruled out given variability in emissions data (±45%). The best linear fit suggests an increase in methyl bromide emissions of 0.3 mg/yr per 1 ppm increase in soil bromide. *Gan et al.* [1998] provide the only other reported study on soil halide concentration effects on methyl halide emissions. They report linear response for emissions from immature potted broccoli plants versus soil bromide concentrations for soils between 0.4 and 100 ppm. While there is a clear positive dependence of methyl bromide emissions on soil bromide concentrations, the dependence may either be linear or follow a stepwise pattern similar to methyl chloride (Figure 8). A minimum emission state followed by a linear increase with soil bromide concentrations after a critical concentration has been reached may be more consistent with the data, as integrated seasonal emissions for all non-salt amended experiments lie between 0.7 and 1.1 mg/m^2 despite sizable differences in soil halide concentrations (Figure 8) [*Redeker et al.*, 2002].

[46] Rice emissions of methyl iodide show an apparently linear response to soil iodide concentration (SIE = 161.4 × [I^-, ppm] +32.5; R^2 = 0.95) (Figure 8). For the observed range of concentrations, methyl iodide emissions increase by 160 mg/yr for every 1 ppm increase in soil iodide.

3.4. Cultivar

[47] Three different seasonal cultivar emissions, measured during the 2001 UCI greenhouse experiment, grown in the same conditions, and corrected for temperature effects are shown in Figure 9. Observed emissions were divided by a factor, based on the ratio of the calculated emissions rate at the recorded temperature during measurement and 30°C, to obtain temperature normalized emission rates.

[48] While daily emission rates were not statistically separable, there were some significant differences in seasonal emissions from cultivar to cultivar. At the 95% confidence level, methyl bromide emissions from M202 were smaller than those of M103 (p = 0.038). Although the emissions of MeBr from the Mars cultivar were the largest, they were not statistically different from M202 emissions beyond the 95% confidence level for a paired student's t-test analysis (p = 0.057). Emissions of methyl bromide from M103 and Mars cultivars were not statistically different (p = 0.241). M103 emissions of methyl iodide were statistically different from those of the Mars cultivar (p = 0.046), but were not statistically separable from methyl iodide emissions from M202 (p = 0.182). Methyl iodide emissions from the M202 cultivar were statistically larger than those from the Mars cultivar (p = 0.004). Owing to large variability of methyl chloride emissions (as reported by *Redeker et al.* [2002]), it is difficult to assess whether methyl chloride emissions depend on cultivar. The high variability of methyl chloride and its marked difference from the plant-based emissions of methyl bromide and methyl iodide [*Redeker et al.*, 2003] further support the hypothesis that methyl chloride emissions are predominantly generated by the soil or the water column and not by the rice plant. Average seasonal emissions of methyl halides from all cultivars were 1.9 ± 3.6, 0.9 ± 0.6, and 65 ± 36 mg/m^2 for methyl chloride, methyl bromide, and methyl iodide, respectively.

[49] To date, all measurements of methyl halide emissions from rice paddies [*Muramatsu and Yoshida*, 1995; *Redeker et al.*, 2000, 2002] fall within the range of emissions shown in the experiments reported here.

3.5. Field/Greenhouse Water-Management

[50] The majority of global rice paddies are irrigated, or flooded continuously throughout the season. A portion of global rice is grown using other field water-management strategies, such as rain-fed and upland rice, which are rarely water saturated and are more often dry. Even when fields are irrigated, choices may be made as to when the fields will be flooded initially and whether or not the fields should be drained for pesticide and herbicide applications. Fields are

Figure 8. Seasonally integrated methyl halide emissions (mg) from M202 studies versus initial soil halide concentration (ppm). Note change in symbols. Here black squares indicate data from Maxwell, California, shaded triangles are data from the second season greenhouse study (2001), and black triangles indicate data from the third, salt-amended greenhouse study (2002). Plotted soil halide concentrations are from the top 10 cm only, as plant uptake of halogens occurs primarily in the early season when root tissue has not penetrated deeply into the soil. Error bars indicate natural variance in emissions and soil halide content. Note differing scales of both *x* and *y* axes for each halide.

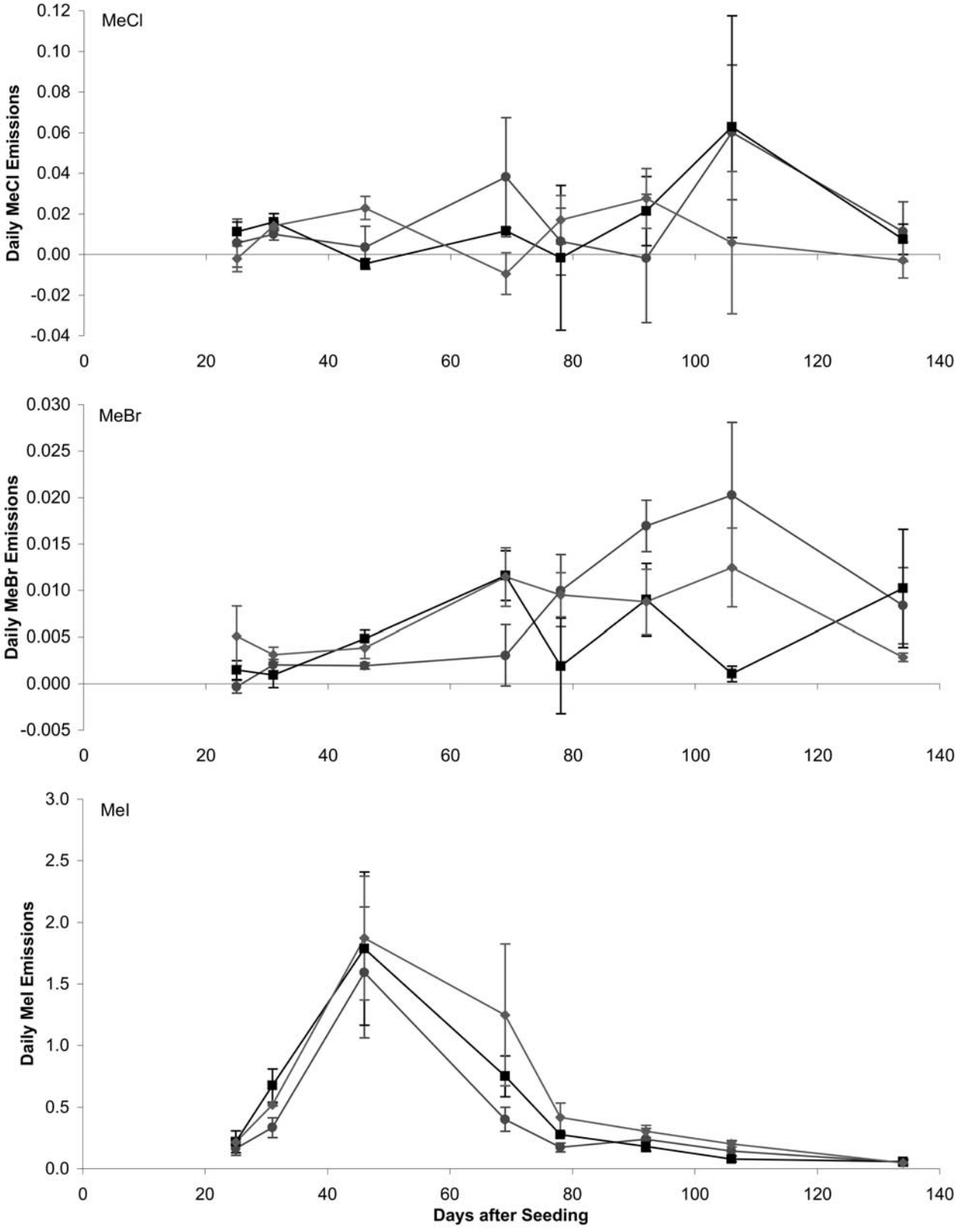

Figure 9. Methyl halide emissions for Mars, M103, and M202 cultivars corrected to 30°C. Symbols are the same as listed in Figure 2. See color version of this figure at back of this issue.

Table 4. Rain-fed and Continuously Flooded Rice Paddy Emission Rates of Methyl Halides[a]

Days After Planting	Cultivar	Average MeCl Emissions		Average MeBr Emissions		Average MeI Emissions	
		Flooded	Rain-fed	Flooded	Rain-fed	Flooded	Rain-fed
78	MARS	6.33E-6	−3.76E-5	1.31E-5	−4.38E-5	6.59E-4	−7.32E-6
	M103	1.71E-5	5.51E-6	7.61E-6	4.01E-6	8.07E-4	7.98E-5
	M202	−1.70E-5	1.00E-5	1.28E-6	3.47E-5	6.14E-4	4.85E-4
92	MARS	−1.96E-5	4.84E-5	1.65E-5	1.31E-5	9.04E-4	1.91E-5
	M103	2.76E-5	2.97E-5	7.77E-6	7.26E-6	1.13E-3	1.95E-5
	M202	2.14E-5	1.66E-4	7.61E-6	4.79E-5	6.29E-4	5.61E-5
106	MARS	6.01E-5	7.71E-5	2.61E-5	2.39E-5	3.47E-4	1.25E-5
	M103	5.81E-6	5.05E-5	1.55E-5	1.57E-5	3.66E-4	4.38E-6
	M202	6.28E-5	−1.56E-5	1.50E-6	3.02E-5	1.29E-4	2.52E-6

Days After Planting	Cultivar	Average of MeCl Flooded Emissions (sd), %	Average of MeBr Flooded Emissions (sd), %	Average MeI of Flooded Emissions (sd), %
All dates	MARS	130	85 (5)	3 (1)
	M103	340 (270)	83 (16)	4 (3)
	M202	770	1800 (600)	30 (25)

[a]Fluxes are given in g m^{-2} day. For flooded rice, n = 3, for rain-fed, n = 1. Values reported as ''average of flooded emissions'' do not include pairs of data where flooded and rain-fed emissions were opposite in sign. Standard deviation of ratio between flooded and rain-fed bins is shown as (sd); standard deviations for flooded bin measurements are shown in Figures 2, 3, and 4.

also drained to allow heavy machinery into the fields for harvest.

[51] During the 1998, 1999, and 2000 field studies, we observed irrigated fields where three separate field water-management strategies were employed: (1) flooded pre-seeding, (2) flooded pre-seeding, but drained during the mid-season, and (3) flooded after seeding. The Maxwell, California, studies measured emissions from fields that were flooded throughout the season (conditions 1 and 2), from before planting until just before harvest, although in 1998 the fields were drained briefly during the tillering phase so that a herbicide could be applied. The Houston 2000 fields were watered sparsely until the rice plants had established themselves (~45 days) and were then flooded for the remainder of the season (condition 3). We have remarked previously on the potential effects of these water-management practices [*Redeker et al.*, 2002]. It appears that the field drainage in Maxwell 1998 slowed the emission rate of methyl iodide and deferred maximum emissions until later in the season (Figure 4). This is more apparent when compared to the 1999 Maxwell season, which was continuously flooded. The delayed initial flooding of Houston paddies is likely to be responsible for the delayed methyl iodide emission maximum (Figure 4).

[52] Agricultural soils have been observed to consume methyl bromide and methyl chloride, with some dependence on soil organic matter concentrations and temperature [*Shorter et al.*, 1995; *Serca et al.*, 1998; *Varner et al.*, 1999a]. It is difficult from these studies to assess the net effect of dry paddies on methyl halide emissions as modifications in field water-management occurred in the early season, before peak emissions of methyl bromide and methyl chloride.

[53] A seasonal study of the effect of unsaturated conditions on methyl halide emissions was performed during the reproductive stage of the second growing season of the greenhouse studies. Three bins leaked sufficiently that they were unable to maintain a constant water level. These bins were watered sporadically throughout the growing season to mimic rain-fed conditions of growth. Each triplicate set of flooded cultivar bins was accompanied by a single unflooded comparison. The results from the three study dates are listed in Table 4, separated by cultivar. The response of both Mars and M103 cultivars to simulated rain-fed conditions is very similar and statistically different to the response of M202 for methyl bromide and methyl iodide.

[54] Methyl iodide emissions are strongly affected during the mid to late season by unsaturated soil conditions. The unflooded M202 cultivar emissions were nearly 30% of the irrigated replicates while rain-fed MARS and M103 cultivars emitted only 3 and 4%, respectively, when compared to their flooded counterparts. Methyl bromide emissions appear to be unaffected by water management for Mars and M103 cultivars; however, the rain-fed M202 cultivar shows an increase over all three sampling dates. It appears that methyl chloride emissions from the rice plant are highly variable and, depending on cultivar, may increase significantly or decrease sufficiently to allow water and plant sinks to overwhelm plant emissions.

[55] The observed differences in how cultivars respond to rain-fed conditions may be due to consistent differences in timing of sampling after soil saturation (i.e., the Mars rain-fed cultivar was sampled consistently at 1 hour post saturation while the M103 cultivar was sampled at 3 hours). Sampling time after soil pore water saturation has been shown to have a strong influence over methyl halide emissions from other soil and plant systems (K. R. Redeker et al., unpublished data).

[56] We conclude that low water conditions strongly inhibit methyl iodide production at all times during the growing season but have little to no effect on methyl bromide and methyl chloride emissions from rice cultivars M103 and Mars. Low water conditions appear to enhance emissions of methyl bromide and methyl chloride from the cultivar M202 while still strongly inhibiting methyl iodide. This further supports the hypothesis, stated by *Redeker et al.* [2000] and explored fully by *Redeker et al.* [2003], that

there are different physiological mechanisms responsible for the emission of each respective methyl halide. There are currently no other reported studies that discuss the impact of water stress on methyl halide emissions from other terrestrial plants or ecosystems. Further research is necessary to accurately determine the effects of various field water-management schemes on methyl halide emissions from rice.

3.6. Aboveground Biomass

[57] Methyl halide emissions are not well correlated with post-season aboveground biomass. Late season emissions, which would be expected to show the highest correlation with late season biomass, do not show any significant trends. This is likely due to the unequal emission potentials of leaf, stem, root and panicle tissues combined with unequal partitioning of plant biomass throughout the season [*Redeker et al.*, 2003]. It is also probable that the homogeneity of the rice paddy system did not provide a large enough variation in aboveground biomass to create significant differences. In either case, because most of the emission potential resides in leaf and panicle tissue, it may be more reasonable to estimate methyl bromide and methyl iodide emissions using leaf area index.

3.7. Calculations of Global Rice Paddy Methyl Halide Emissions

3.7.1. A Revised Estimate

[58] Global estimates of methyl halide emissions have been difficult to assess in the past as the information regarding the systems studied (soil halides, pore water content, ambient air, soil and water temperatures, aboveground biomass) was incomplete. This difficulty was compounded by a limited understanding of the components of the system that were most influential in determining methyl halide emissions. Previous global ecosystem estimates were based entirely on global surface area covered by an ecosystem multiplied by emissions averages. These estimates did not incorporate any detail regarding temperature, growth stage, pore water content, or soil halide content.

[59] Our previous estimates of global methyl halide emissions were based on M202 cultivar studies primarily and included data taken from various temperature regimes. They include emissions from the water column of the rice paddy, which have been shown to be equal to approximately 100, 10, and 1% of the seasonal emissions of methyl chloride, methyl bromide and methyl iodide, respectively, from rice paddies [*Redeker et al.*, 2000, 2002]. Assuming an average ambient temperature of 30°C in rice paddies, we can start an extrapolation based on the temperature scaled M202 emissions observed in the 2001 greenhouse.

[60] Since different cultivars exhibited slightly different capacities to emit methyl halides, M202 emissions will be scaled to ''average rice'' emissions by multiplying methyl bromide and methyl chloride fluxes by factors of 1.29 and 0.86, respectively. M202 emits methyl iodide at the average rate of the three cultivars studied.

[61] Approximately 62% of the world's rice is grown under constantly flooded conditions (irrigated and deepwater rice) while 38% of global rice is grown in undersaturated soil conditions (rain-fed and upland rice) [*IRRI*, 1995]. According to the reported results, it is necessary to multiply the methyl iodide emissions by a factor of $0.66 \pm = 0.62 \times 1.0 + 0.38 \times 0.1$) to account for diminished methyl iodide production in undersaturated conditions.

[62] Global rice paddy soil halide concentrations are not well quantified. Our results, combined with data from *Yuita* [1994a, 1994b] and *Bradford et al.* [1996] suggest that halides are likely to be much less concentrated in paddy soils than in nearby non-paddy soils. According to *Yuita* [1994a, 1994b] soil chloride, bromide, and iodide concentrations in rice paddy soils are diminished by a factor of 2, 20, and 25 compared to regional soils. Soil iodide concentrations in Maxwell, California, were 0.06 ppm while regional Californian soils average 0.4 ppm, a factor of 7 more concentrated than the paddy soils. Assuming that paddy soils are generally 2, 7, and 15 times less concentrated than regional soils in chloride, bromide, and iodide and taking the reported average global soil halide concentrations (100, 32, and 3.9 mg/kg for chloride, bromide, and iodide, respectively) from *Graedel and Keene* [1996] and *Kabata-Pendias and Pendias* [1992], average paddy halide concentrations of 50, 4.5, and 0.25 ppm Cl-, Br-, and I-, respectively, are estimated.

[63] If these soil halide concentrations are used to calculate methyl halide emissions using the linear fits described earlier in the soil halides section, seasonally integrated emissions of 4.1, 1.8, and 72.9 mg/m^2/yr for methyl chloride, methyl bromide, and methyl iodide are obtained. When the conversion factors for irrigated area and cultivar are included, the expected methyl halide emissions from rice paddies are 3.5, 2.3, and 48 mg/m^2/yr at 30°C ambient temperature. Finally, when seasonal emissions are multiplied by the global land area devoted to rice agriculture (1.51×10^{12} m^2, Statistics Norway, Statistical YearBook 1998 (http://www.ssb.no/english/yearbook/1998/tab/t1510002.shtml)), the annual methyl halide emissions from global rice paddies are equal to 5.3, 3.5, and 72 Gg/yr for methyl chloride, methyl bromide, and methyl iodide. These results provide 0.1%, 1.6%, and 4.5% of the total sources necessary to balance the quantified global methyl chloride, bromide, and iodide sinks.

3.7.2. Error Analysis

[64] A comprehensive discussion of emissions uncertainties is premature; however, an estimate may be attempted through the data presented here. Our estimate of fields grown under different water management styles is accurate according to reports from 1995 [*IRRI*, 1995]. Assuming a conservative shift of 10% of global rice paddy water management toward more or less irrigation, this would lead to an error of ±15% in the methyl iodide estimate. Taking the worst case scenario from our cultivar study, we can assign a potential error of ±50% to all methyl halide emissions from rice based on cultivar differences.

[65] Soil chloride, bromide, and iodide concentrations in studied commercial fields range from 25% to 200% our estimated global means [*Redeker et al.*, 2002; *Yuita*, 1994a, 1994b]. Soils from more coastal regions may be significantly more enriched than the reported fields, so a conservative estimate of the range of potential soil halides is 25% to 200% our estimate. This creates an error in emissions of

methyl chloride of −200 to +600%, −80 to +110% for methyl bromide, and −40 to +55% for methyl iodide.

[66] The global temperature estimate of 30°C is likely to be high, but a conservative range of possible field temperatures is 20° to 35°C. This would lead to errors in our estimate of −130 to +65%, −70 to +35%, and −60 to +30% for methyl chloride, methyl bromide, and methyl iodide, respectively.

[67] When these errors are combined (total error = $\sqrt{\Sigma \text{error}_i^2}$), the global estimates, including error, are equal to 5.3 (range −7.6 to 37.4), 3.5 (range −0.6 to 7.9), and 72 (range 8 to 131) Gg/yr for methyl chloride, methyl bromide, and methyl iodide.

3.8. Conclusions

[68] A total of four rice cultivars were examined over six growing seasons. Increased ambient air temperature, soil pore water saturation, and soil halide concentration all led to increased methyl halide emissions in controlled greenhouse experiments. The effects of these secondary factors are generally an order of magnitude smaller than the changes associated with or imposed by the growth stage of the rice. Although the influence of temperature on methyl bromide and methyl iodide emissions remains positively correlated throughout the season, temperature response changes with growth stage. Temperature response is not identical between methyl halides. Rice cultivars have slightly different seasonally integrated emissions for methyl bromide and methyl iodide. Rice paddy emissions are insensitive to light levels and, within the homogeneous rice paddy ecosystem, aboveground biomass.

[69] Methyl iodide is emitted during the early stages of rice growth (30 to 35% of season duration), before maximum tillering, while methyl bromide emissions peak after the reproductive stage has begun, between 60 and 70% of the season. Generally, methyl chloride emissions are not affected by growth stage of the rice plant.

[70] Methyl bromide emissions during the tillering and reproductive stages appear to be driven by similar mechanisms because the slope of the temperature response remains constant. Once the ripening phase begins MeBr emissions are not affected by temperature increases. The temperature effect for methyl bromide in the Mars cultivar is more severe than the response shown by M103 and M202 cultivars. Temperature dependences for methyl iodide do not follow the same patterns as methyl bromide emissions. Tillering stage dependences differ from those of the reproductive and ripening stages. As with methyl bromide, the Mars cultivar shows a stronger response to elevated temperatures throughout the season. Our studies show no effects from increased or decreased light levels.

[71] All methyl halide emissions are increased when rice is grown in soils with elevated soil halide concentrations. Methyl chloride and methyl bromide emissions may have stable emission rates for soil chloride and bromide concentrations lower than some critical threshold (between 60 and 90 ppm for Cl^- and 3 and 11 ppm for Br^-), while methyl iodide emissions appear to be linear with soil iodide concentrations. More measurements will need to be made to determine the precise nature of methyl chloride and methyl bromide responses to elevated soil halides.

[72] Of the three cultivars studied simultaneously during the second season greenhouse, M103 emitted more methyl iodide than Mars and M202. M202 emitted less methyl bromide than the other two cultivars. These effects may be linked to differences in temperature dependences between cultivars. Rain-fed or undersaturated soils inhibit methyl iodide production during the early season by decreasing the rate of plant growth and continue to have a significant impact on methyl iodide emissions during later stages of growth. The process by which soil pore water saturation affects methyl iodide production from rice in the later season is not clear. More research is needed to quantify the effects of field water-management practices on methyl halide emissions.

[73] Average emissions of 3.5, 2.3, and 48 mg/m^2/yr of MeCl, MeBr and MeI are calculated, with higher emissions of methyl iodide in flooded regimes. This translates to global emissions of 5.3 ± 15.9, 3.5 ± 4.2, and 72 ± 61 Gg/yr methyl chloride, methyl bromide, and methyl iodide, respectively. These emissions are small compared to methyl chloride emissions from shrublands, wetlands, coastal salt marshes, rapeseed agriculture, and fungi (40 to 170 Gg/yr methyl chloride), but similar in scale to emissions from these ecosystems for methyl bromide (0.9 to 14 Gg/yr methyl bromide) [*Dimmer et al.*, 2001; *Gan et al.*, 1998; *Lee-Taylor and Holland*, 2000; *Rhew et al.*, 2000, 2001; *Varner et al.*, 1999b; *Watling and Harper*, 1998]. Studies of methyl iodide emissions from these ecosystems are limited, but emissions from wetlands and peatlands (8.8 Gg/yr methyl iodide) appear to be much smaller than emissions from rice paddies. It is likely that many of the estimates of ecosystem emissions from these other ecosystems will change when the effects of temperature, light, growth stage, soil halide content, and soil pore water are taken into account.

[74] The emissions we calculate will not reduce the discrepancy between sources and sinks in global methyl halide budgets. Emissions of methyl chloride and methyl bromide from rice paddies, in particular, are minor components of their respective cycles. Emissions of methyl iodide remain high, and are surprisingly robust for all parameters studied. The errors associated with this study, within a very homogeneous ecosystem, point out the difficulty in extrapolation of emissions from other, less homogeneous, ecosystems.

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Figure 1. The 2001 UCI greenhouse. Bins are filled with Mars, M202, and M103 cultivars.

Figure 2. Averaged methyl chloride emissions data from all studies. Open and solid black squares represent M202 cultivar studies. Open squares represent differing conditions of growth: during the 1998 and 1999 Maxwell seasons open squares indicate rice results from Burnt Straw fields, while in the 2002 greenhouse, they represent rice grown in soil amended with salt. Red triangles indicate unplanted control plots in all studies. Dark blue open circles represent the cultivar Cocodrie and solid blue circles represent the Mars cultivar. Dark purple diamonds represent M103, a commonly grown cultivar in California. Figures 2a and 2d have two replicates per data point, while Figures 2b, 2c, 2e, and 2f have triplicate analyses. All graphs are at the same scale except Figure 2f. Error bars represent 1 standard deviation.

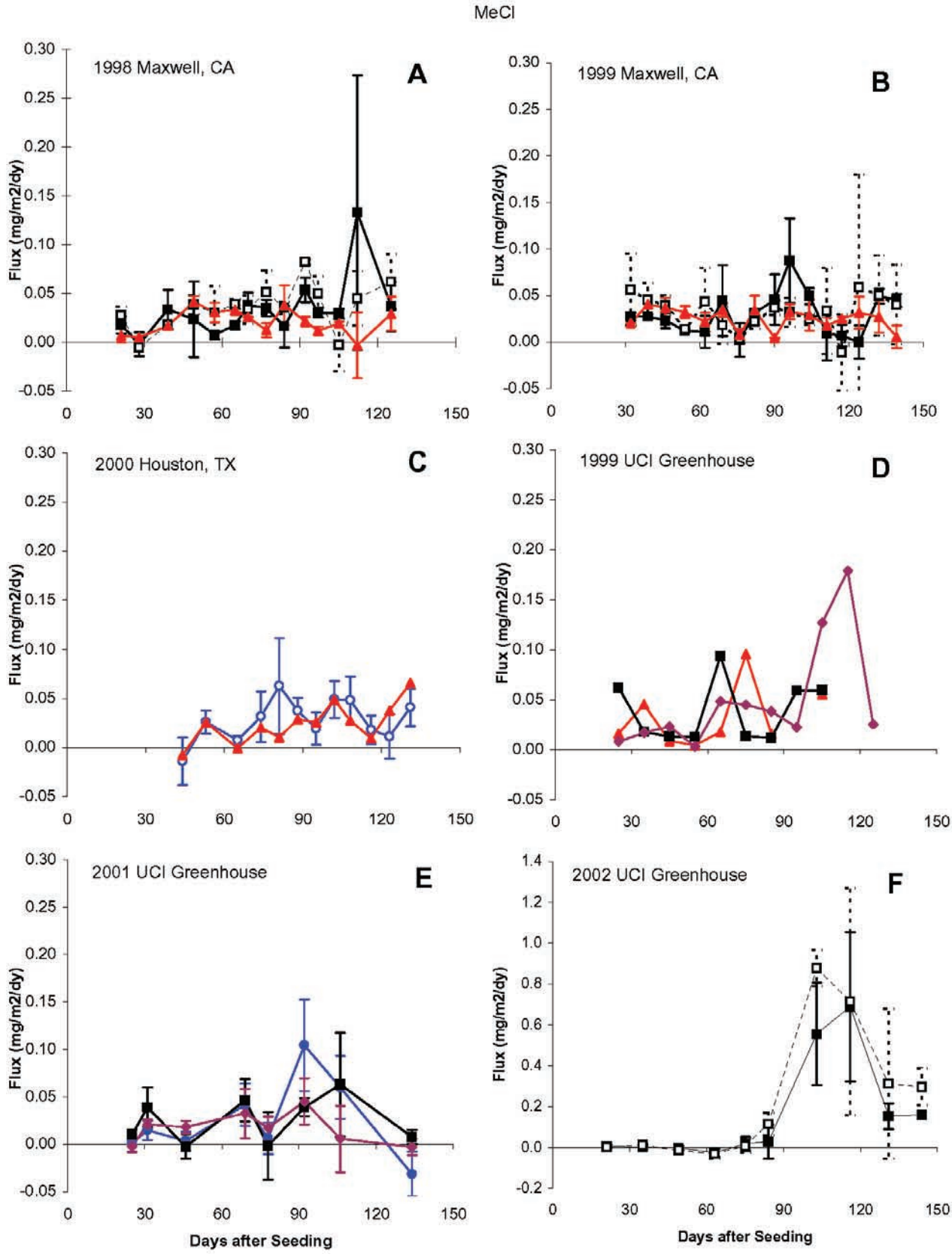
MeCl
1998 Maxwell, CA
A
1999 Maxwell, CA
B
2000 Houston, TX
C
1999 UCI Greenhouse
D
2001 UCI Greenhouse
E
2002 UCI Greenhouse
F
Flux (mg/m2/dy)
Days after Seeding

Figure 2.

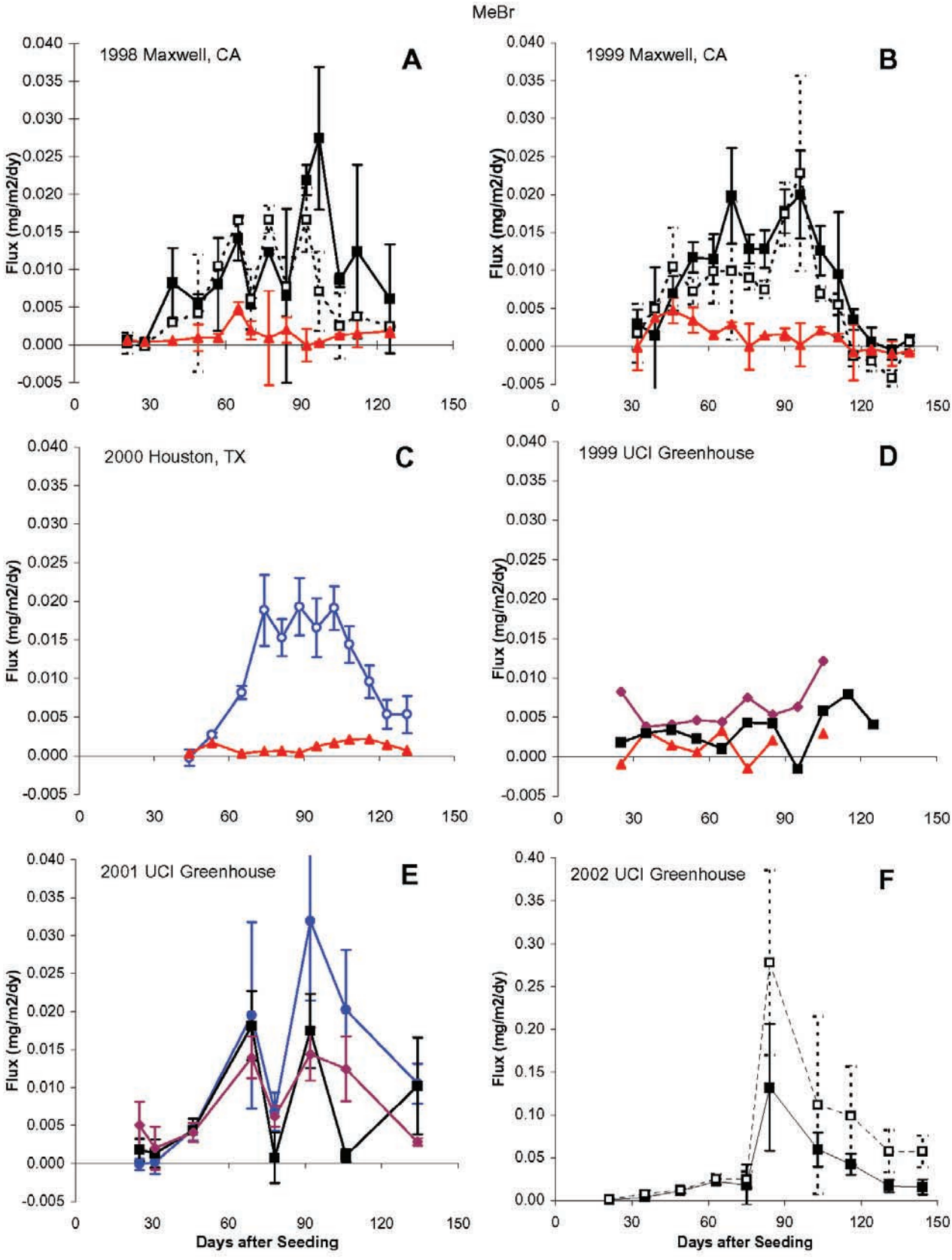

Figure 3. Results for methyl bromide as described for Figure 2.

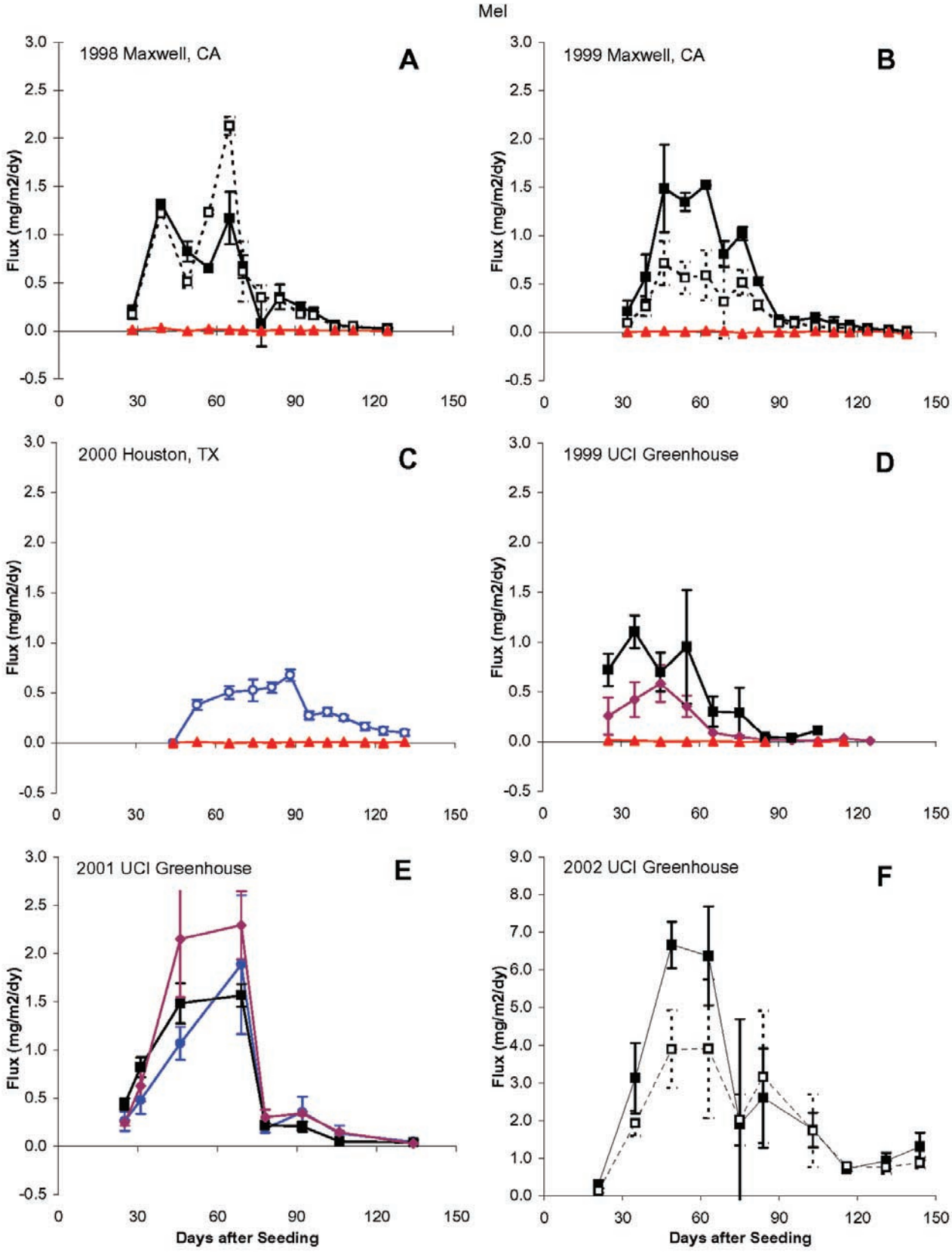

Figure 4. Results for methyl iodide as described for Figure 2.

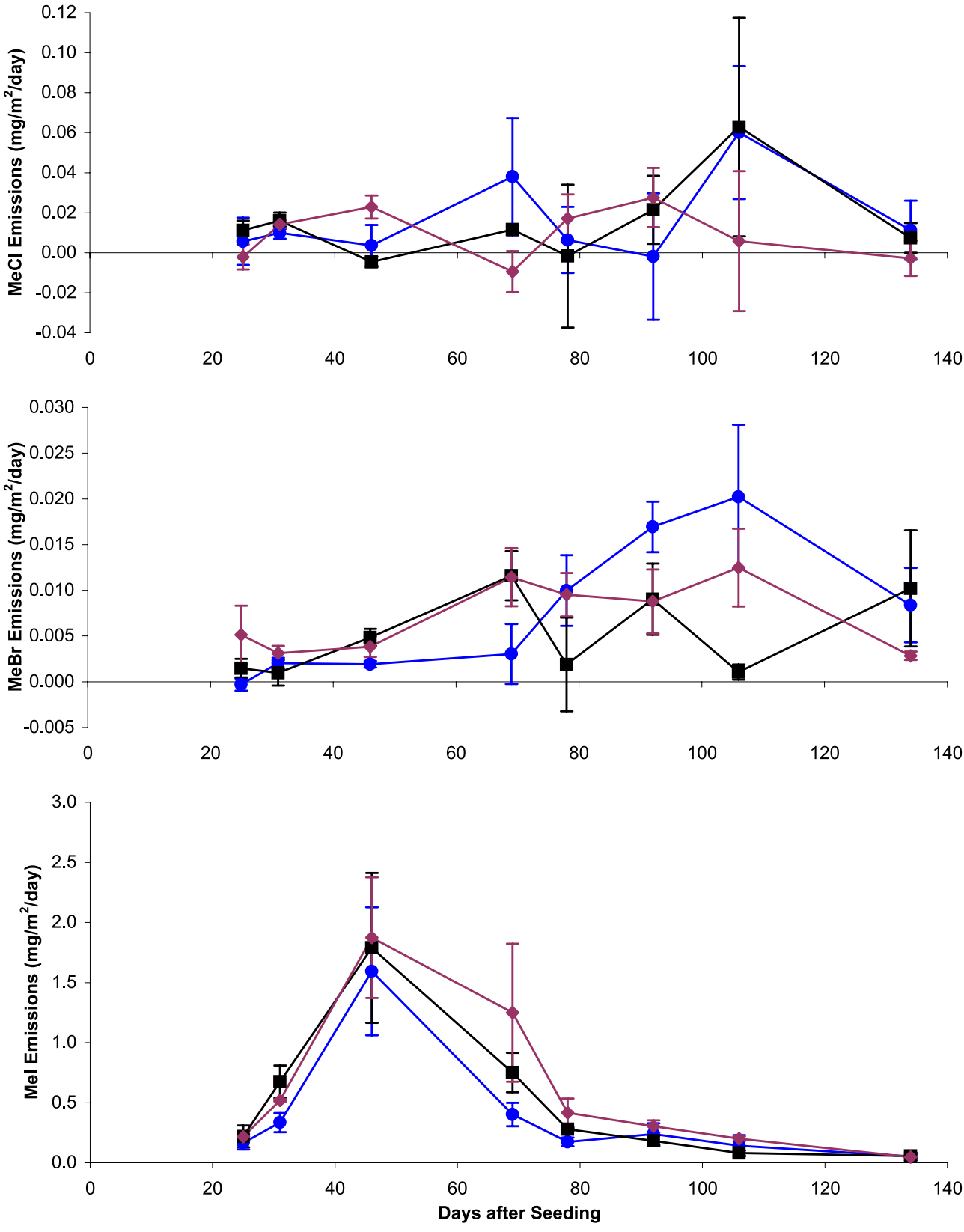

Figure 9. Methyl halide emissions for Mars, M103, and M202 cultivars corrected to 30°C. Symbols are the same as listed in Figure 2.