

## Seasonal mass balance of halogens in simulated rice paddies

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[1] Halogens released from soil reservoirs to the atmosphere play important roles in atmospheric chemistry, including ozone loss and aerosol formation. Closed system experiments to determine controlling factors in halogen movement between the pedosphere, hydrosphere, terrestrial biosphere, and atmosphere are needed. This paper presents results from a closed system experiment on simulated rice paddies. It was observed that most water-extractable (bioavailable), halogens were swept downward from the surface during the initial watering pulse (~50, 70, and 75% of chloride, bromide, and iodide in unadulterated soils). Soil halogens were sequestered by rice plants with 28, 4, and 24% of the remaining bioavailable chlorine, bromine, and iodine processed by the plant tissue by the end of the season. Of the bioavailable halogens taken into the rice plant, less than 1% of chlorine or bromine is volatilized as a methyl halide while over 90% of iodide is emitted as gaseous CH<sub>3</sub>I. **INDEX TERMS:** 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0330 Atmospheric Composition and Structure: Geochemical cycles; 1615 Global Change: Biogeochemical processes (4805); 1610 Global Change: Atmosphere (0315, 0325); 1890 Hydrology: Wetlands. **Citation:** Redeker, K. R., S. L. Manley, L. Brothers, K. McDuffee, M. Walser, and R. J. Cicerone (2004), Seasonal mass balance of halogens in simulated rice paddies, *Geophys. Res. Lett.*, 31, L11504, doi:10.1029/2004GL019579.

### 1. Introduction

[2] Halogen cycles influence stratospheric ozone loss, tropospheric aerosol formation, and tropospheric oxidative capacity [Vogt *et al.*, 1999; O'Dowd *et al.*, 2002; Montzka *et al.*, 2003]. The terrestrial biosphere is influenced by soil halogens as either micronutrients at low concentrations, or toxic agents at high concentrations [Yuita, 1994; Rupe *et al.*, 2000].

[3] Relatively little is known about the influence of the terrestrial biosphere on halogen partitioning between pedosphere, hydrosphere, and atmosphere. A current assumption appears to be that the biosphere has very little effect on halogen transport through soils [Oberg, 2002], which has led to the use of bromide as a tracer for hydrological transport studies [Bronswijk *et al.*, 1995].

[4] Here we present results from simulated rice paddies constructed in the University of California, Irvine (UCI)

greenhouse. After initial halide conditions were set, additional input of halogens was minimized, providing a closed experiment where the transport of halogens from the soil to the water, plant, or atmosphere could be observed, allowing us to accurately assay the relative importance of various processes within rice paddies.

[5] Presented is an empirical, systematic, mass balance for chloride (Cl<sup>-</sup>), bromide (Br<sup>-</sup>), and iodide (I<sup>-</sup>) in the experimental rice paddies and a discussion of the implications for commercial field halide concentrations. These results provide a gross estimate for the relative importance of various processes in halogen cycling for other ecosystems.

### 2. Methods

[6] The greenhouse at UCI was fitted with six glass bins. Each bin (0.91 m × 0.91 m × 0.6 m) was filled with soil with a consistency similar to that found in commercial paddy fields. The depth of the bins was sufficient for unimpeded rice root growth. The UCI experimental marsh provided the soil, which was sifted through a 1/2" mesh and filled to a depth of ~30 cm (~340 kg processed soil) in each bin.

[7] Fertilizer (NH<sub>4</sub>NO<sub>3</sub>, ~15 g-N per bin), and salt (NaCl, NaBr and NaI; 200, 6.0, and 0.15 g halide per bin, respectively) when appropriate, was added to the soil and mixed in a commercial cement mixer for homogeneity. Bin soil halide concentrations were similar to global paddy concentrations for unsalted bins and to upland, non-paddy soils for the amended soil bins [Yuita, 1994]. Further details of the UCI greenhouse can be found in Redeker *et al.* [2004].

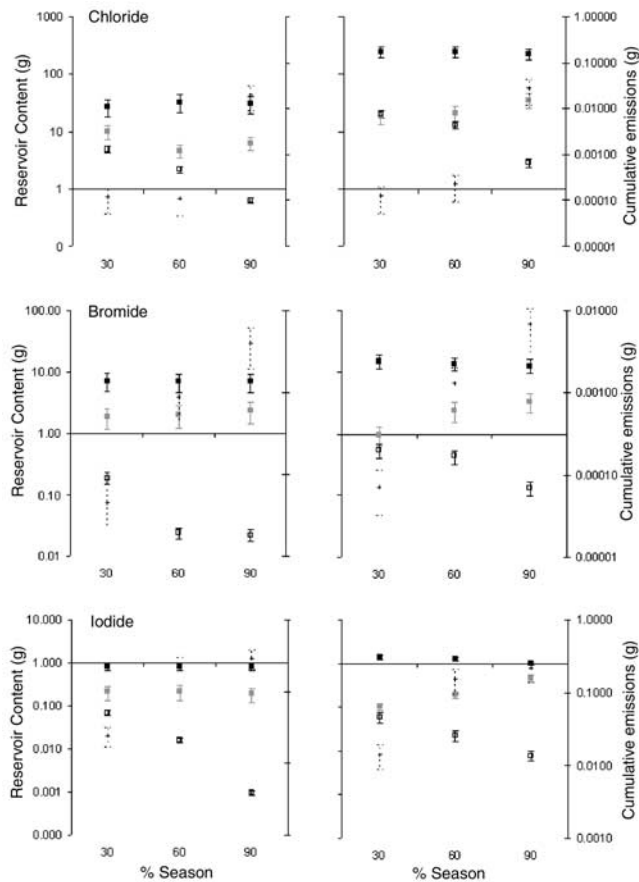
[8] M202, a commonly grown commercial cultivar subspecies of *O. sativa japonica*, was grown in unsalted, flooded soils in three glass bins lined with rubber pond lining while three identically lined bins contained M202 cultivar rice grown in salt amended, flooded soils. Rice densities in greenhouse bins were similar to those in commercial paddy fields. Field water management was identical to that in Maxwell, CA commercial rice paddies [Redeker *et al.*, 2000]. Rice biomass was determined through a complete harvest at the end of the season, and through representative (2–3 plants) harvests during the season.

[9] Soil cores (5 cm diameter) were taken at three stages, during maximum growth (vegetative stage), reproduction (flowering), and during ripening/senescence. Cores were 12–26 cm long and were separated into two sections, 0–10 and 10+ cm. Soils were dried to constant weight and processed for storage as described in Redeker and Cicerone [2004]. Soil halide concentrations were obtained as described in Redeker and Cicerone [2004]. Note- our soil halide concentrations were determined via a low impact

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**Figure 1.** Total halides (grams) in various reservoirs are shown at three stages of growth during the season (30, 60, and 90% of the season duration, equivalent to tillering, reproductive and ripening stages). Chloride data is shown in the top row, followed by  $\text{Br}^-$  and  $\text{I}^-$ . Salt amended data is shown in the right column, unamended soils in the left column. Each halide is shown with identical logarithmic scales between salted and unsalted soils while scales are not identical between halides. Error bars indicate one standard deviation ( $n = 3$ ). Soils are shown by filled squares, with gray indicating the surface soils (0–10 cm) and black the bottom soils (10–29 cm). Water is shown by open black squares, while emissions from the rice plant are indicated by black crosses. Rice plant emissions are also shown in the right-hand side y-axis, while soil and water contents are shown on the left-hand y-axis.

(water rinsed three times) removal process, which we believe is representative of bioavailable halide concentrations. Soil halide adsorption depends on soil pH, temperature and pore water saturation [Yuita *et al.*, 1991]. In irrigated rice paddies up to 50% I, 20% Br, and 100% of Cl will easily dissolve [Yuita *et al.*, 1991]. The remainder of soil halides are in recalcitrant forms, bound organically or inorganically, with uncertain mobilization time-frames.

[10] Biomass for each component of rice plant tissue was estimated based on end of season biomass totals and general trends of rice biomass growth. These estimates are similar to data from RICE [1967] and values measured during the season [Redeker *et al.*, 2004]. Tissue preparation was

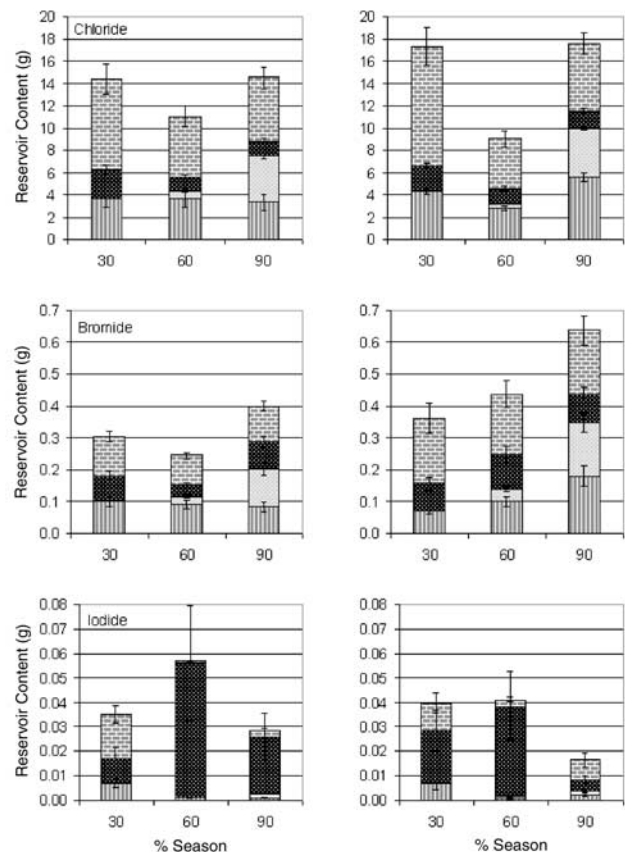
described in Redeker *et al.* [2004], as was Gran's technique, which was used for halide concentration measurements.

### 3. Results and Discussion

[11] Mass balances for  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ , calculated from estimated biomass (gdwt) and measured soil, water, and plant tissue concentrations are shown in Figures 1 and 2. Standard deviations for each set of reservoir measurements are shown, with  $n = 3$  for all reservoirs. Approximately 90% of total sample variance was due to natural variance within the sample pool. Only ~10% derived from instrumental or methodological variance. Instrumental precision for halide determination was 9%, 17% and 13% for  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ , respectively. Halides within simulated rice paddies were calculated to be “balanced” (equivalent between the beginning and the end of the season) when variances for  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  in each reservoir were taken into consideration.

#### 3.1. The Soil Column

[12] The homogeneously distributed soil halides were swept downward during the first watering, as expected for highly soluble, anionic tracers [Bronswijk *et al.*, 1995]. Later, halides moved toward the surface of the soil, so that by the end of the season there was a concentration bulge



**Figure 2.** Total halides (in grams) in various plant reservoirs at three stages of growth during the season. Error bars indicate one standard deviation ( $n = 3$ ). Gray vertical lines, light gray stipple, black stipple, and gray brick indicate leaf, panicle, root, and stem tissue.

near 25 cm depth that was discernible to both pore-water analysis and end of the season soil cores (auxiliary material<sup>1</sup>). 25 cm depth  $\text{Cl}^-$  pore-water concentrations at season's end were 140 and 10 mM in amended and non-amended bins as opposed to the surface pore-water concentrations of 25 and 2 mM. Pore-water  $\text{Br}^-$  concentrations increased by a factor of three from the surface to the bottom (with maximum concentrations of 3.0 mM in salt amended bins, 1.0 mM in non-amended bins) while  $\text{I}^-$  concentrations were enhanced by nearly a factor of 5 (maximum concentrations were equal to 0.20 mM). Soil halide concentrations calculated from pore water concentrations, using water weight to estimate water content and assuming all halides were in solution, were similar to concentrations in soils obtained from soil cores at the end of the season.

[13] To account for the halides in the bottom of the bins (which were not obtained through soil cores during the early season) we assumed that total bin halides were well represented by soil halide, water halide and plant tissue halide concentrations at the end of the season. Early season 10–30 cm concentrations were calculated to be equal to the bin halide mass at the end of the season, subtracting the early season 0–10 cm halide amount. This assumption should have a minimal effect on the results as most plant uptake of halides occurred during the early season and appeared to be primarily from the surface 10 cm of soil [Redeker and Cicerone, 2004].

[14] Salt-amended soils were affected to a greater degree than the non-amended soils as the added salt would have dissolved and leached with the addition of water. The percentage of  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  remaining in the surface 10 cm (halides found in supernatant water, surface 10 cm soil, plant tissues, and volatilized) at first sampling (30% of seasonal duration, SD) was 52, 25, and 29% for non-amended soils, and 19, 11, and 14% for amended soils (Figure 1).

[15] The halide gradient formed at the beginning of the season prompted movement of halides from the bottom of the bins toward the surface (auxiliary material). This effect was more pronounced in salt-amended bins, as surface soil halide content rose, from the beginning to the end of the season, by factors of 2, 3, and 5 for  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ , respectively. Halide content of surface soils in non-amended bins remained nearly constant after the first sampling.

[16] These results suggest that in irrigated rice paddies (~60% of global rice area with similar concentrations to non-amended bins) a large portion (50–70%) of initial bioavailable soil halide content will be swept away by initial field flooding.

### 3.2. The Water Column

[17] Water added to greenhouse bins was processed through reverse osmosis and charcoal filters. Added water was below detection limits for all halides; 35  $\mu\text{M}$   $\text{Cl}^-$ , 2.0  $\mu\text{M}$   $\text{Br}^-$ , and 50 nM  $\text{I}^-$ . All halides found in supernatant water in the greenhouse were presumed to come from the soil column. Early season halide content of overlying water in the bins was high, 1.25 versus 5.10 mM  $\text{Cl}^-$  in non-amended versus amended bins, 21.5 versus 61.5  $\mu\text{M}$   $\text{Br}^-$ , and 5.0 versus 4.3  $\mu\text{M}$   $\text{I}^-$ . By mid-season (60% SD) and

thereafter water column halide concentrations had dropped to 0.17 versus 0.72 mM  $\text{Cl}^-$ , 2.5 versus 15.1  $\mu\text{M}$   $\text{Br}^-$ , and 0.07 versus 0.57  $\mu\text{M}$   $\text{I}^-$ , respectively for non- and salt-amended bins (Figure 1).

[18] An initial pulse of halide rich water may be expected in rice paddy run-off but salt removal from and deposition to the paddy through irrigation runoff should equilibrate by early to mid-season. Irrigation water may be halide rich and might act as a source of halides to the plants and soil column over the course of the season.

### 3.3. The Plant

[19] Rice plants proved to be efficient excavators of halides from surface soils. Root tissue in all bins extended to 10 cm, with few roots extending further. Halogens removed from bin soils (0–29 cm); to be stored in plant tissue or volatilized, were equivalent to 28%, 4%, and 24% of the bioavailable  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  that remained in non-amended soils after flooding. In salt-amended soils 6%, 4%, and 14% of the bioavailable  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  was removed. Within the halide-depleted surface soils (<10 cm), the rice plant excavation efficiency was even higher; ~50%, 20%, and 55% of bioavailable  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ .

[20] Figure 2 shows the movement of halogens through plant tissues over the course of the season. Total  $\text{Cl}^-$  content in rice tissue was nearly identical at the end of the season when compared to the early season; however a decrease in  $\text{Cl}^-$  content during the reproductive phase (60% SD) was observed. This drop cannot be explained through sample variance, and no metabolic mechanism is known that requires rice to diminish  $\text{Cl}^-$  content during mid-season. It is possible that there are several pools that were not adequately represented in our analyses; e.g., the root tissue collected at 60% SD may not have been as comprehensive at the collections at 30 and 90% due to concerns regarding the effect of complete removal on other plants within the chamber. This would under represent root biomass, which could explain total plant decreases in  $\text{Cl}^-$  and  $\text{Br}^-$ . Alternatively, flowers were assumed to be minor components of panicle biomass and were not measured; they may have carried a substantial load of  $\text{Cl}^-$  and  $\text{Br}^-$  that would have been under represented in the panicle halogen pool.

[21] Total  $\text{Cl}^-$  in rice grown in salted soils was statistically identical to the  $\text{Cl}^-$  content of rice grown in non-amended soils. Total leaf  $\text{Cl}^-$  remained nearly constant, while root  $\text{Cl}^-$  decreased even as root mass increased (Figure 2). The increase in panicle  $\text{Cl}^-$  was entirely due to the weight of the developing grain and most panicle  $\text{Cl}^-$  appeared to be transferred from the root and stem reservoirs (Figure 2).

[22] Total plant  $\text{Br}^-$  appeared to increase over the course of the season. As with  $\text{Cl}^-$ , total leaf  $\text{Br}^-$  remained constant during the early- to mid-season but late season leaf  $\text{Br}^-$  increased in salt-amended bins, while it remained constant under non-amended conditions. Stem  $\text{Br}^-$  appeared to remain stable, as did root  $\text{Br}^-$ . Like  $\text{Cl}^-$ , panicle  $\text{Br}^-$  increased in proportion to panicle weight (Figure 2), although with panicle  $\text{Br}^-$  the stem and root reservoirs did not appear to be the halide source. Total plant  $\text{Br}^-$  was not well correlated with available soil  $\text{Br}^-$  (Figures 1 and 2).

[23] Unlike the other halides, 92% of  $\text{I}^-$  taken into the plant was volatilized as methyl iodide (MeI), while  $\text{Cl}^-$  and  $\text{Br}^-$  (0.02 and 1.0% volatilized) were mostly stored in plant

<sup>1</sup>Auxiliary material is available at <ftp://ftp.agu.org/apend/gl/2004GL019579>.

tissue. Iodide content in tissues was the most variable of the halides. During the early season, while the rice was most actively volatilizing  $I^-$  in the form of MeI [Redeker et al., 2004], stem and leaf  $I^-$  concentrations were highest (Figure 2). After the greatest MeI emissions, stem and leaf  $I^-$  reservoirs were severely diminished while the root  $I^-$  reservoir was equal to the entire early season plant  $I^-$  content. As the season ended, and MeI emissions diminished, leaf and stem  $I^-$  concentrations increased and root  $I^-$  content dropped. Variance in  $I^-$  for rice plant tissue was very large, especially at the end of the season. The large reservoir of root  $I^-$  in non-amended soils shown in Figure 2 was likely due to root access to highly concentrated regions of soil  $I^-$  (inherent soil heterogeneity due to small amount of added NaI).

[24] Rice grown in enhanced halide soils had statistically identical halide concentrations as rice grown in low, natural concentrations for the majority of the growing season [Redeker et al., 2004]. Rice plants did not take up halides in proportion to their soil halide concentration ratios [Redeker et al., 2004]. These results suggest that rice plants maintained constant  $Cl^-$  and  $Br^-$  concentrations within their tissues. As further support for this hypothesis, Figure 2 shows that plant-based  $Cl^-$  and  $I^-$  removal efficiency decreased from unsalted to salted bins, while  $Br^-$  removal efficiency remained the same.  $Cl^-$  and  $I^-$  concentrations within the plant may have reached a maximum value while  $Br^-$  concentrations may not have, which allowed the plant to continue removing and storing bromide, potentially in place of  $Cl^-$  and  $I^-$ . These results may have implications for halide toxicity in paddy fields.

### 3.4. Rates of Input and Removal of Halogens From Irrigated Rice Paddies

[25] Graedel and Keene [1996] calculated an average deposition of  $0.25 \text{ g m}^{-2} \text{ yr}^{-1}$   $Cl^-$  to continental surfaces, mainly as sea spray deposition. This flux is larger in coastal regions, with a maximum input of  $10 \text{ g m}^{-2} \text{ yr}^{-1}$  recorded along the Norwegian west coast [Oberg, 2002]. Our observed removal rate of  $Cl^-$  from paddy soils is  $14.5 \text{ g m}^{-2} \text{ yr}^{-1}$ . Results calculated from non-amended bins show that, if rice consistently excavates halides and there are no halogen inputs other than rainfall, a little less than 4 years would be required to remove bioavailable  $Cl^-$  from the top meter of soil, 25 years for  $Br^-$  and 4 years for  $I^-$ . Recall that our extraction method was a “soft” extraction by water, which may leave up to 95, 80 and 20% of soil  $I^-$ ,  $Br^-$ , and  $Cl^-$  in recalcitrant forms [Yuita et al., 1991]. The dissolution rate of these recalcitrant forms is uncertain, although however rapidly they may be accessed, the removal rate of halogens from rice paddies is still rapid. At best, addition of the entire recalcitrant pool of halogens delays full  $Cl^-$ ,  $Br^-$  and  $I^-$  extraction by 1, 20, and 95 years.

[26] Because halide concentrations in commercial paddy soils are not zero, even after decades of rice growth [Redeker et al., 2000] halides removed from the system by rice must be replaced through some mechanism. Aerosol and dry deposition are unlikely to be sufficient [Muramatsu et al., 1996; Oberg, 2002]. Irrigation water is a source of halogens, especially in regions where water has traveled far enough for significant evaporation to occur. Many nitrate and phosphate fertilizers contain low levels of halogen salts,

and in some regions salt fertilizers are directly applied. Burning of rice-crop stubble, while volatilizing up to  $0.2 \text{ g m}^{-2} \text{ yr}^{-1}$  of plant tissue  $Cl^-$  in the form of  $CH_3Cl$  [Redeker et al., 2003], may return the majority (>98%) of tissue  $Cl^-$  back to the soil. This mechanism of return will not apply in regions where rice straw is harvested, to be burned in biomass reactors. Further research into halide replenishing mechanisms will need to be performed to obtain a full understanding of halide transport in rice paddies. Also, more research on the continued efficiency of halogen removal over long time scales is needed to fully address the implications of crop growth on global halogen cycles.

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