

# UC Irvine

## UC Irvine Previously Published Works

### Title

Atmospheric methyl halides and dimethyl sulfide from cattle

### Permalink

<https://escholarship.org/uc/item/8mn2910w>

### Journal

Global Biogeochemical Cycles, 13(2)

### ISSN

0886-6236

### Authors

Williams, Jody  
Wang, Nun-Yii  
Cicerone, Ralph J  
[et al.](#)

### Publication Date

1999-06-01

### DOI

10.1029/1998gb900010

### Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

## Atmospheric methyl halides and dimethyl sulfide from cattle

Jody Williams,<sup>1</sup> Nun-Yii Wang, and Ralph J. Cicerone

Earth System Science, University of California, Irvine

Kazuyuki Yagi

Japan International Research Center for Agricultural Sciences, Tsukuba, Japan

Mitsunori Kurihara and Fuminori Terada

National Institute of Animal Industry, Tsukuba, Japan

**Abstract.** We have measured emissions of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $(\text{CH}_3)_2\text{S}$  (DMS) from Holstein cows. In one experiment, two cows were studied in separate metabolic research chambers for a 24-hour period while on a normal diet and were studied for an additional 24-hour period 1 week later after being placed on a diet enhanced in chloride and bromide. Methyl chloride emissions ranged between  $0.4 \times 10^{-3}$  and  $1.5 \times 10^{-3}$  g  $\text{cow}^{-1} \text{d}^{-1}$ , while methyl bromide emissions were much smaller,  $3 \times 10^{-6}$ – $2 \times 10^{-5}$  g  $\text{cow}^{-1} \text{d}^{-1}$ . Daily emissions of methane from these cows were 134–180 g  $\text{cow}^{-1} \text{d}^{-1}$ , quite similar to values found in many previous studies. A second 24-hour study of two different cows on normal diets yielded daily emissions of  $0.6 \times 10^{-3}$  and  $0.9 \times 10^{-3}$  g  $\text{CH}_3\text{Cl}$ ,  $0$ – $1.0 \times 10^{-6}$  g  $\text{CH}_3\text{Br}$ , and 191 and 176 g  $\text{CH}_4$ . If these emissions of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  are representative of the 1.3 billion head of cattle worldwide, then the global source of atmospheric  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  from cattle would be 0.23–0.70 Gg  $\text{yr}^{-1}$  and  $(1$ – $10) \times 10^{-3}$  Gg  $\text{yr}^{-1}$ , respectively. These emissions of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  represent  $<0.02\%$  and  $<0.005\%$ , respectively, of the total annual global atmospheric sources of these compounds; therefore, emissions of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  from cattle are insignificant contributors to their total sources. Discovered serendipitously, DMS emissions were between 0.17 and 0.24 g  $\text{cow}^{-1} \text{d}^{-1}$ , and chloroform emissions were  $2 \times 10^{-4}$ – $3 \times 10^{-3}$  g  $\text{cow}^{-1} \text{d}^{-1}$ . DMS from cattle is not a major source over hemispheric or global scales but could be important in certain geographical regions. Chloroform ( $\text{CHCl}_3$ ) emissions were similarly detected and quantified, as were those of  $\text{C}_2\text{H}_5\text{X}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ).

### 1. Introduction

The budgets of atmospheric  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  are not well established. Perhaps the most useful constraint on the total annual sources or sinks is the relationship between the atmospheric residence time  $T_r$ , the global atmospheric burden  $B$ , and sources or sinks; that is,

$$\text{sources} = \text{sinks} = B/T_r \quad (1)$$

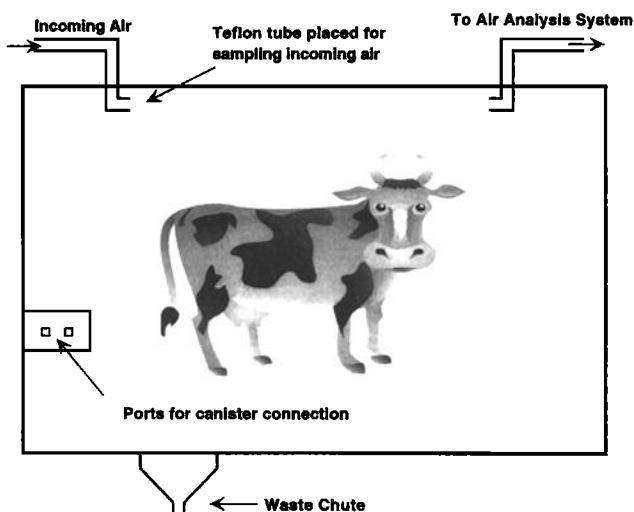
Equation (1) is only approximately true for several reasons; it assumes steady state and that the gas in question is well mixed. Equation (1) is more accurate for gases with  $T_r$  greater than the time constant for exchange between the Northern and Southern Hemispheres, which is about 0.8 year [Prather *et al.*, 1987]. The most reliable quantity in (1) is the atmospheric burden: 145 Gg of  $\text{CH}_3\text{Br}$  (1 Gg =  $10^9$  g) and 5000 Gg of  $\text{CH}_3\text{Cl}$  (these data are from Butler [1994], Khalil *et al.* [1993], and Singh *et al.* [1983] and are probably accurate to within 15%).

Current information implies that  $T_r$  is  $\sim 0.7$  years for  $\text{CH}_3\text{Br}$

[Yvon-Lewis and Butler, 1997]. If this is true, global sources must be  $\sim 205$  Gg  $\text{yr}^{-1}$  in steady state. Independent estimates of  $\text{CH}_3\text{Br}$  sources can be obtained by studying the sources themselves or by equating to sinks which can also be estimated separately; such studies suggest that there may be an unidentified (predominantly northern) source of  $\text{CH}_3\text{Br}$  of about 90 Gg  $\text{yr}^{-1}$  [Yvon-Lewis and Butler, 1997]. Alternatively, current sink estimates may be too large; for relevant data and discussion of individual sources and sinks, see Yvon and Butler [1996] and Butler and Rodriguez [1996]. Briefly, major sources are thought to be biomass burning and emissions from fumigated agricultural soils. The burning of leaded gasoline as a source is highly uncertain, and the world's oceans appear to be a net sink for atmospheric  $\text{CH}_3\text{Br}$  [Lobert *et al.*, 1995; Yvon and Butler, 1996; Yvon-Lewis and Butler, 1997].

For atmospheric  $\text{CH}_3\text{Cl}$ ,  $T_r$  is  $\sim 1.5$  years, implying that total sources must be 3.5 Tg  $\text{yr}^{-1}$  (1 Tg =  $10^{12}$  g). Weisenstein *et al.* [1992] calculated a residence time of 1.6 years, but OH amounts derived from atmospheric trends and lifetimes of  $\text{C}_2\text{H}_3\text{Cl}_3$  [Prinn *et al.*, 1995] imply a slightly shorter lifetime. Emissions of  $\text{CH}_3\text{Cl}$  from biomass burning worldwide have been estimated as 1.3 ( $\pm 0.2$ ) Tg  $\text{yr}^{-1}$  [Andreae *et al.*, 1996]. Previously, oceanic emissions were thought to account for the largest source of  $\text{CH}_3\text{Cl}$ , 1.7–2.4 Tg  $\text{yr}^{-1}$  [Tait *et al.*, 1994] and 5 Tg  $\text{yr}^{-1}$  [Singh *et al.*, 1983]; however, recent evidence suggests this source to be 0.2–0.4 Tg  $\text{yr}^{-1}$ , which is only 6–12% of

<sup>1</sup>Now at Department of Environmental and Chemical Sciences, Chapman University, Orange, California.



**Figure 1.** The volume of the cow chamber was 14,000 L. The air flow rate through each chamber was controlled as described in the text. A teflon tube was placed inside the pipe which directed the incoming air, and the other end was connected to a port located on the side of the chamber. This allowed sampling of the air just before entering the chamber. The other port was used to sample air in the chamber. The gas-analysis system monitored oxygen, carbon dioxide, and methane. Wastes were dropped through an opening on the floor just behind the cow leading to a waste-separating device on the floor below.

the total [Moore *et al.*, 1996]. Thus, at present, we have unsatisfactory understanding of the sources and possibly the sinks of these methyl halides; identified sources of  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  do not appear to be enough to explain their atmospheric amounts.

The possibility that a significant  $\text{CH}_3\text{Br}$  source is yet unidentified and the fact that  $\text{CH}_3\text{Cl}$  sources are not well studied led us to ask if emissions of these gases from cows could be important. Several facts led to this idea. First, the rumen (a part of the digestive system of ruminant animals like cows) functions as a continuous fermentor; anaerobic microbes permit relatively efficient energy extraction from low-grade, high-cellulose food. Fermentation products include acetate, propionate, butyrate,  $\text{CO}_2$ , and  $\text{CH}_4$ . Methane production by cows is reasonably well quantified [Kleiber *et al.*, 1945; Atlas and Bartha, 1981; Crutzen *et al.*, 1986]. Could the bromide and chloride in grasses, grains, and other forages be methylated in the rumen and emitted as  $\text{CH}_3\text{X}$  (where  $X = \text{Br}$  or  $\text{Cl}$ )? Bromide fractions vary in grains, grasses, and clover between  $\sim 1$  and 40 ppm (by dry weight) and are generally 0.001–0.01 as large as those of chloride [Kabata-Pendias and Pendias, 1992]. The worldwide cattle population is  $\sim 1.3 \times 10^9$  [United Nations, 1995], and typical daily food intakes are 3–9 kg (dry weight), so total dry matter consumption is of the order of  $3 \times 10^{12}$  kg  $\text{yr}^{-1}$ . Thus, for example, if all of the dietary bromide were converted to  $\text{CH}_3\text{Br}$  and emitted, the source could be  $\sim 35$  Gg  $\text{yr}^{-1}$  of  $\text{CH}_3\text{Br}$  with 10 ppm bromide in the feed and 3.5 Gg  $\text{yr}^{-1}$  if 1 ppm is in the feed. We find no scientific literature on emissions of  $\text{CH}_3\text{X}$  from cows and almost no information on the fate of dietary chloride and bromide [see, e.g., Hungate, 1966, National Research Council (NRC), 1988]. There is some information available on the physiological functions of chloride in cattle and on dietary requirements, but there is little or

none for bromide [NRC, 1988]. Interestingly, bromochloromethane ( $\text{CH}_2\text{BrCl}$ ) as a dietary additive suppresses methanogenesis [McCrabb *et al.*, 1997, and references therein], but there appear to be no reports of the *in vivo* production of halogenated methanes.

With such a dearth of information in the scientific literature, a direct experimental approach seemed necessary. Accordingly, we decided to mount experiments to quantify these emissions, using existing chambers where cows are studied under controlled conditions; in such experiments, considerable benefit can be drawn from knowledge of methane emissions. By placing a cow inside a chamber of known volume and measuring the ventilation rate of the chamber and the amount of each gas of interest in the chamber, one can calculate the cow's emission of each gas. In the course of our research on the methyl halides, we discovered emissions of dimethyl sulfide (DMS), chloroform ( $\text{CHCl}_3$ ), and chloroethane and bromoethane,  $\text{C}_2\text{H}_5\text{Cl}$  and  $\text{C}_2\text{H}_5\text{Br}$ , respectively.

## 2. Experiment

The experiments were conducted at the National Institute of Animal Industry, Ministry of Agriculture, Forestry and Fisheries in Tsukuba, Japan, in the Energy Metabolism Laboratory. Cows were placed in separate flow-through type chambers [Iwasaki *et al.*, 1982] where the flow rate, temperature, and humidity were monitored every 5 min. The concentrations of oxygen, carbon dioxide, and methane in each chamber were also measured at 5 min intervals by a gas-analyzing system. Figure 1 illustrates such a chamber and its configuration. During each experiment, the airflow through the 14,000 L chamber was controlled at rates listed below and varied  $< 1.5\%$ . Animal wastes dropped through a  $40 \times 70$  cm opening beneath the hindside of the cow which led to a separating device on the floor beneath the chamber. This device separated the wastes according to urine and feces. Samples of the chamber air were taken from several ports located on the side of the chamber where evacuated canisters could be connected. In order to sample the air prior to entry into the chamber, a teflon tube was connected from the location of the air inflow to one of the ports on the side of the chamber. The sample canisters consisted of 1.4-, 2-, 6-, and 8-L stainless steel canisters and 2-L aluminum canisters.

These samples were then shipped to the University of California at Irvine for analysis. Of each sample, 250 mL were preconcentrated at 142 K in a glass-bead packed stainless steel sample-injection loop immersed in an *n*-pentane/liquid nitrogen bath, thermally desorbed, and directly injected onto a  $25 \text{ m} \times 0.53 \text{ mm}$  Poraplot-Q column (Chrompack). Detection was by mass spectrometry (UNICAM automass model 150) in the selective ion-monitoring mode (mass charge ratio ( $m/z$ ) = 50 for  $\text{CH}_3\text{Cl}$  and  $m/z$  = 94 for  $\text{CH}_3\text{Br}$ ). Varying amounts of calibration gas (9.68 ppb  $\text{CH}_3\text{Br}$  and 479 ppb  $\text{CH}_3\text{Cl}$  from Scott Specialty Gases) were used to build a calibration curve, excellent linearity was achieved over the range of 0.31–1.03 ng for  $\text{CH}_3\text{Cl}$  and 9.5–48.5 pg for  $\text{CH}_3\text{Br}$ .

The amount of gas  $X$  emitted by the study cow in a 24-hour period is the difference of two terms, namely, the amount of gas  $X$  leaving the chamber in the outward flow  $F_o$ , minus the amount of gas  $X$  entering the chamber in the incoming flow  $F_i$ . That is,

$$\text{emissions per day} = \int_0^{24} f_{\text{chmbr}}(t) F_o(t) dt - \int_0^{24} f_{\text{ia}} F_i(t) dt \quad (2)$$

where  $f_{\text{chmbr}}$  is the mole fraction of gas  $X$  measured in the chamber at time  $t$  and  $f_{\text{ia}}$  is the mole fraction of gas  $X$  measured in the incoming air at time  $t$ . This expression can be simplified because  $F_o(t) = F_i(t) = F$ , in particular,

$$\text{emissions per day} = F \int_0^{24} [f_{\text{chmbr}}(t) - f_{\text{ia}}(t)] dt \quad (3)$$

Three separate experiments were conducted. The first, in April 1996, used cows 309 and 339 in 24-hour studies with regular diets described in Table 1. Immediately following the first experiment with the regular diet, sodium halide (NaBr and NaCl) solution was added to each cow's diet by pouring the solutions into a port on the side of the cow leading to the rumen for 8 days prior to the second experiment to check if emissions were elevated (see Table 1 for amounts). Standard Japanese grasses have ~20 ppm bromide and ~5000 ppm chloride [Yuita, 1983]. Thus, for example, if a cow would eat ~7300 g food  $\text{d}^{-1}$ , this intake would include 0.15 g bromide  $\text{d}^{-1}$  and 37 g chloride  $\text{d}^{-1}$ . We decided to increase these values 10 times, i.e., 1.5 g bromide  $\text{d}^{-1}$  and 370 g chloride  $\text{d}^{-1}$ . Because the cows' health may be affected by such high levels of chloride, only half of this amount was used, i.e., 185 g chloride [Ministry of Agriculture, Forestry and Fisheries, 1994]. In the second experiment the cows' emissions were again monitored for a 24-hour period to test if the halomethanes were enhanced because of added sodium halides. The amounts and type of feed and sodium halide quantities added to the cows' diet are shown in Table 1.

In the April 1996 study, we took 119 samples, but we discarded 20 of them for the following reasons. In the first experiment (i.e., regular diet), at different times of day, we sampled chamber air simultaneously with pairs of evacuated flasks. In each case, one flask was simply filled to ambient pressure, and the other was pressurized to  $1.7 \times 10^{-5}$  pascal, with a teflon-valved oilless, greaseless compressor (KNF Neuberger). In six cases of these paired samplings the unpressurized flask yielded higher concentrations than its pressurized replicate. Pressurized samples are more reliable in analyses of this type (because the number of contained gas molecules exceeds the number of active surface sites of the canister walls), so we discarded the measurements from unpressurized flasks that did not agree with their pressurized partners. Because these six flasks were

**Table 1.** Holstein Cows' Diet and Body Weight in April 1996

Cow	Body Weight, kg		Feed,* kg $\text{d}^{-1}$	Added Chloride,† g $\text{d}^{-1}$	Added Bromide,† g $\text{d}^{-1}$
	April 9, 1996	April 18, 1996			
309	642	658	8.06	185	1.5
339	678	703	8.44	185	1.5

Cows 309 and 339 were 10 and 8 years of age, respectively.

\* Feed consists of 50% Orchardgrass hay, 25% Italian ryegrass hay, and 25% perennial ryegrass hay.

† Sodium halide solution was added every day from April 10 to April 18, 1996.

**Table 2.** Holstein Cows' Diet and Body Weight in June 1997

Cow	Age, years	Body Weight, Kg June 10, 1997	Feed*, kg $\text{d}^{-1}$
434	5	565	9.45
956	4	487	8.27

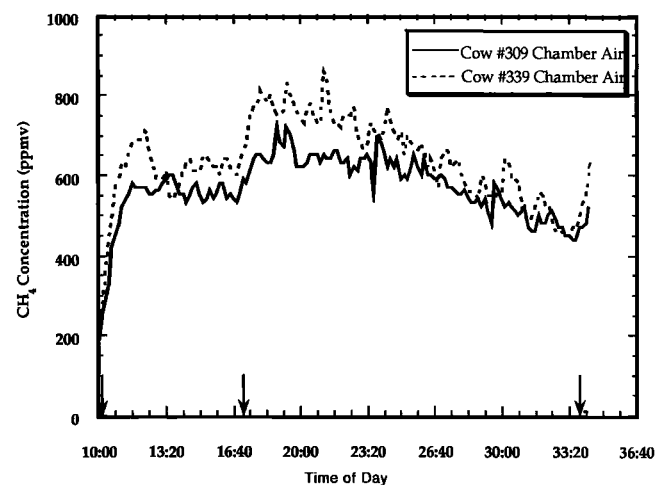
\* Feed is Italian ryegrass hay wafers.

from a batch of new flasks that had not been tested adequately before deployment, 11 other data points from such flasks were also discarded. Three other data points were discarded for other reasons; for example, MeBr concentrations were higher in incoming air than in the chamber, and no replicate sample was available. The other trace gases studied were not affected.

The third and final experiment was conducted in June 1997 on two different cows, 434 and 956, whose sizes and diets are described in Table 2. During the June 1997 experiment, we took ~20 pressurized samples and none were discarded.

Previous studies of  $\text{CH}_4$  emissions from cattle indicate that  $\text{CH}_4$  concentrations generally peak ~1.5 hours after feeding, and Figure 2 shows the measured time evolution of methane amounts in the chambers during the studies of cows 309 and 339. Accordingly, we devised a 24-hour sampling schedule that was guided by the cows' feeding schedule with more sampling when peak emissions of  $\text{CH}_4$  were expected.

Many previous studies have found that methane emissions from cows depend on body weights, ages, daily food-intake amounts, and other factors [see, e.g., Hungate, 1966; Crutzen *et al.*, 1986; McCrabb *et al.*, 1997]. Typical daily emissions of  $\text{CH}_4$  per animal are 230 g (dairy cows), 178 g (cattle on feed), and 148 g (cattle on range), so emissions from cows 309 and 339, i.e., 157.80 and 180.10 g  $\text{CH}_4 \text{d}^{-1}$  (Table 3), are similar to values found in previous studies. In addition, cow 339 was fed more than cow 309, since cow 339 was larger in size. This may partly explain the difference in emissions between the two cows. Methane emissions from cow 434 and cow 956 (Table 4) also fall into this same range. The data in Table 3 show that



**Figure 2.** Methane concentrations measured versus time in the flow-through chambers for cows 309 and 339 with the regular diet in 1996 experiment. Methane amounts in incoming air were less than 2 ppm. Arrows note each time the cow was fed. Note methane peaks in the chamber air after each feeding.

**Table 3.** Trace Gas Emissions in April 1996 Experiments

Species	Regular Diet, g d <sup>-1</sup>		Halide Diet, g d <sup>-1</sup>	
	Cow 309	Cow 339	Cow 309	Cow 339
(CH <sub>3</sub> ) <sub>2</sub> S	0.24	0.22	0.21	0.17
CHCl <sub>3</sub>	0.85 E-03	3.2 E-03	0.28 E-03	1.5 E-03
CH <sub>3</sub> Br	6.9 E-06	2.6 E-06	2.0 E-05	3.8 E-06
CH <sub>3</sub> Cl	1.5 E-03	0.49 E-03	1.4 E-03	0.41 E-03
CH <sub>4</sub>	158	180	134	163

$E - n = 10^{-n}$ .

CH<sub>4</sub> emissions were enhanced for both cows 309 and 339 with the regular diet compared to the halide diet.

It is possible that some of the observed elevation in concentration measured in the chambers for the gases of interest was due to gases produced in the waste reservoirs beneath the floors of the chambers. However, note that concentrations of each gas increased just after feeding times (Figures 2–6), implying that direct emissions from the cows were dominant. To investigate the possibility of significant emission from the dropped animal wastes, we performed experiments on the waste reservoirs after the June 1997 chamber studies. The reservoir beneath cow 434 collected 29 kg of waste (wet weight), while the reservoir beneath cow 956 collected 21.6 kg. We covered these waste reservoirs and extracted air samples

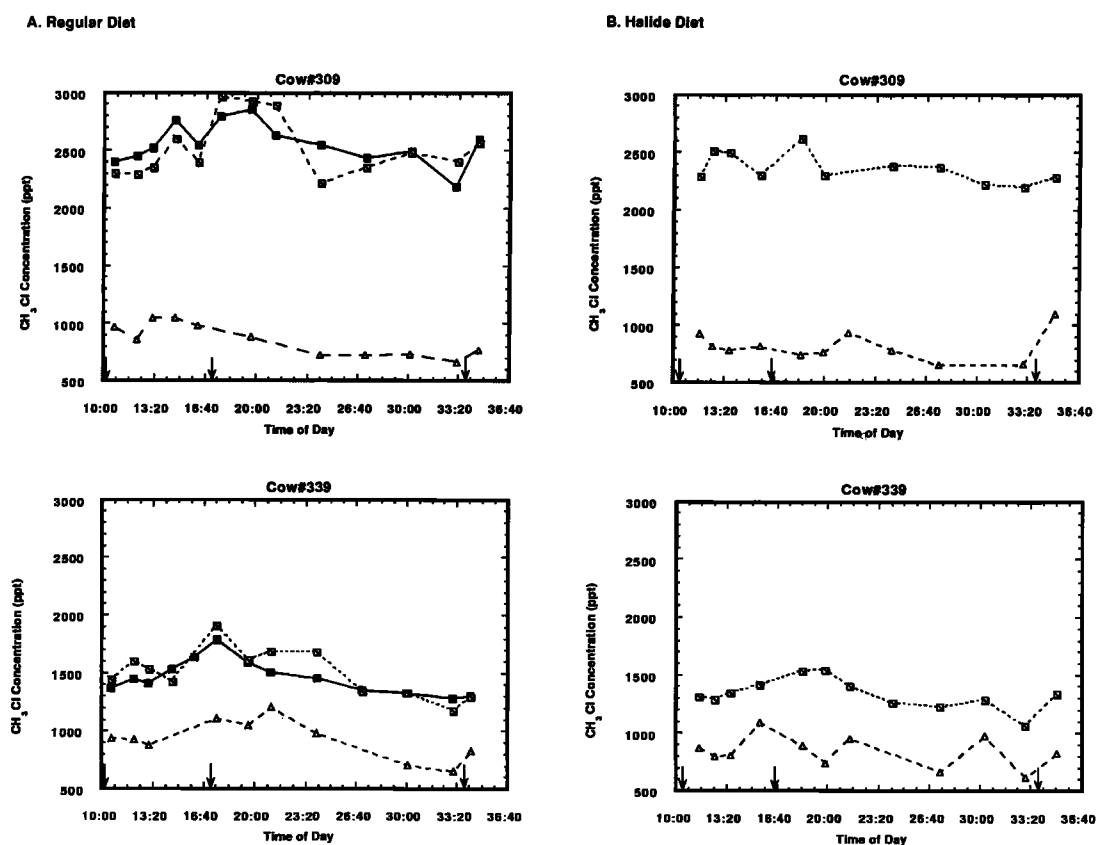
**Table 4.** Trace Gas Emissions in June 1997 Experiments

Species	Cow 434	Cow 956
(CH <sub>3</sub> ) <sub>2</sub> S	not measured	not measured
CHCl <sub>3</sub>	not measured	not measured
CH <sub>3</sub> Br	1.0 E-06	0
CH <sub>3</sub> Cl	0.9 E-03	0.6 E-03
CH <sub>4</sub>	191	176
C <sub>2</sub> H <sub>5</sub> Cl	0.45 E-03	0.05 E-03
C <sub>2</sub> H <sub>5</sub> Br	3.1 E05	0

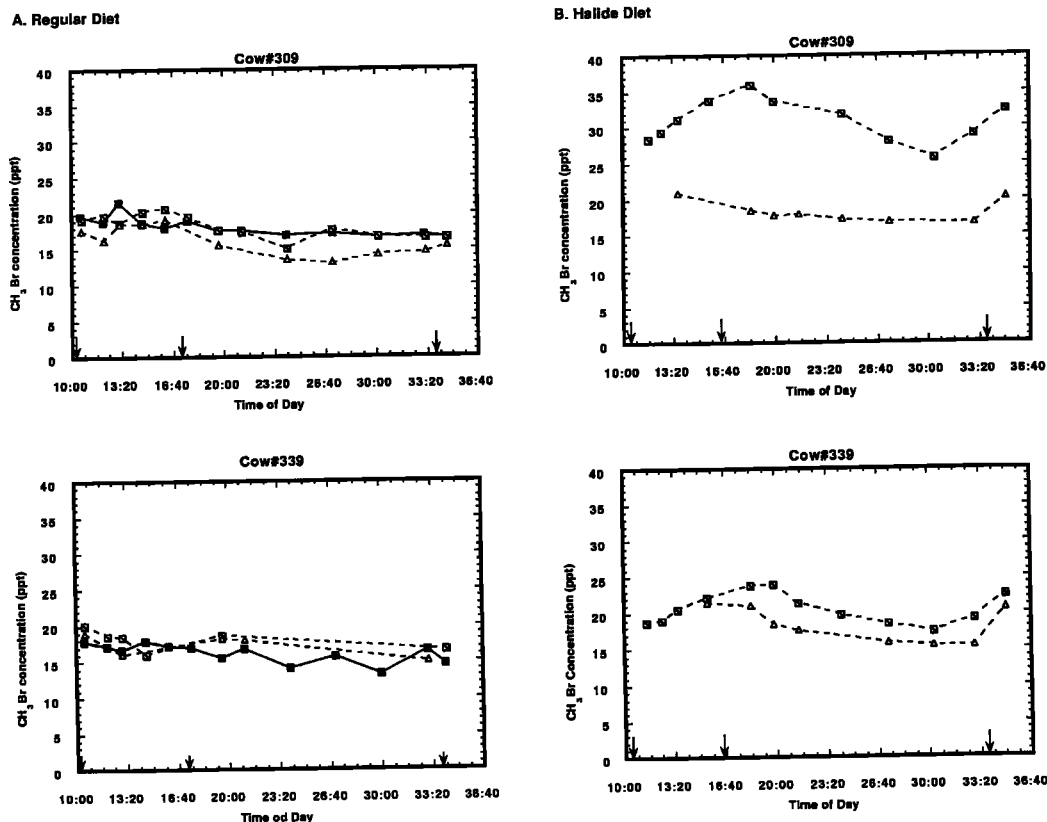
$E - n = 10^{-n}$ . Emissions are given in grams per day.

after 1 hour and 2 hours; no measurable increases with time were observed for CH<sub>3</sub>X (X = Cl or Br). C<sub>2</sub>H<sub>5</sub>X concentrations did increase above background levels but not greatly. Accordingly, we will use (3) above as if direct emissions of gases from the cows caused the elevated concentrations in the metabolic chambers even though gases lost from the wastes dropped by each cow could have added slight amounts to those emitted directly.

During sample analysis when we operated the Gas Chromatograph/Mass Spectrometer in its full-scan mode, we discovered unknown gases which we identified to be DMS and chloroform. We subsequently used mass 62 and mass 47 in the single ion-monitoring mode for DMS and CHCl<sub>3</sub>, respectively. Because no standard was available to determine the DMS and



**Figure 3.** Measured methyl chloride concentrations in the flow-through chambers for cows 309 and 339 for the (a) regular diet and the (b) halide diet. Two sets of chamber air samples were taken for the regular diet experiment. One set of canisters was pressurized (solid square with solid line), and the other set was unpressurized (open slashed square with dashed line). The canisters used to sample the air just before entering the chamber (incoming air, triangle with dashed line) were unpressurized. Arrows represent each time the cow was fed.



**Figure 4.** Measured methyl bromide concentrations in the flow-through chambers for cows 309 and 339 for the (a) regular diet and the (b) halide diet. Two sets of chamber air samples were taken for the regular diet experiment. One set of canisters was pressurized (solid square with solid line), and the other set was unpressurized (open slashed square with dashed line). The canisters used to sample the air just before entering the chamber (incoming air, triangle with dashed line) were unpressurized. Arrows represent each time the cow was fed.

$\text{CHCl}_3$  concentrations, we ratioed peak areas to  $\text{CH}_3\text{Cl}$  mass 50 using the Scott standard. Finally, the fragmentation of each was accounted for with data from the literature to arrive at a concentration estimate [Mass Spectrometry Data Centre, 1974].

### 3. Results and Discussion

The concentrations of  $\text{CH}_3\text{Cl}$  measured in the chambers during the April 1996 experiments are shown in Figure 3. The regular diet experiment showed  $\text{CH}_3\text{Cl}$  emissions of  $1.48 \text{ mg d}^{-1}$  from cow 309 and  $0.49 \text{ mg d}^{-1}$  from 339. With the halide diet, cow 309 emitted  $1.4 \text{ mg d}^{-1}$ , and cow 339 emitted  $0.41 \text{ mg d}^{-1}$  (Table 3). Individual data points from the June 1997 experiment are not shown here, but they were of very high quality, and the 24-hour integration with (3) yielded emissions of  $0.86$  and  $0.57 \text{ mg CH}_3\text{Cl}$  per day for cows 434 and 956, respectively, as listed in Table 4.

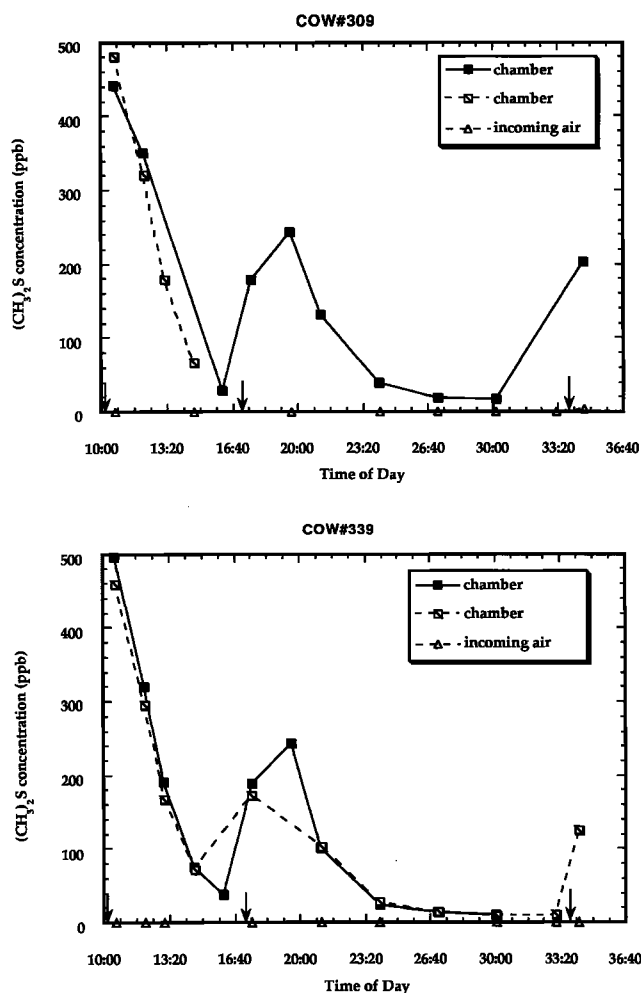
Methyl bromide concentrations measured versus time in the April 1996 experiments are shown in Figure 4. The halide diet experiment showed elevated  $\text{CH}_3\text{Br}$  emissions with both cows 309 and 339 with respect to the regular diet, i.e.,  $20.2 \times 10^{-6}$  and  $3.76 \times 10^{-6} \text{ g d}^{-1}$  compared to  $6.89 \times 10^{-6}$  and  $2.51 \times 10^{-6} \text{ g d}^{-1}$  (Table 3).

Data from June 1997 are not shown here but their quality exceeded those of April 1996 and the application of (3) to them yielded 24-hour integrated emissions of  $1.04 \times 10^{-6} \text{ g d}^{-1}$

for cow 434 and no measurable emissions for cow 956 in June 1997.

Using a global cattle population of 1.3 billion, the calculated global source of  $\text{CH}_3\text{Cl}$  from cattle is  $0.23\text{--}0.70 \text{ Gg yr}^{-1}$ . A total annual global source of  $3.5 \text{ Tg CH}_3\text{Cl yr}^{-1}$  can be estimated by dividing the atmospheric burden ( $1.05 \times 10^{11} \text{ mol}$ ) by its atmospheric residence time (1.5 years). If our data for  $\text{CH}_3\text{Cl}$  emissions from cows are representative of the world's 1.3 billion head of cattle [United Nations, 1995], these animals would only be responsible for  $<0.02\%$  of the total annual global source. Therefore cattle are not a significant source of methyl chloride. Despite elevated emissions with added bromide, the calculated range for the  $\text{CH}_3\text{Br}$  source strength from cows,  $(1.2\text{--}10) \times 10^{-3} \text{ Gg yr}^{-1}$ , is not significant considering total sources of  $\sim 205 \text{ Gg yr}^{-1}$ .

Dimethyl sulfide (DMS) showed elevated concentrations immediately following each feeding in both April 1996 experiments for both cows (Figure 5). The emission rate of DMS for cows 309 and 339 was  $2.43 \times 10^{-1}$  and  $2.26 \times 10^{-1} \text{ g d}^{-1}$ , respectively, for the regular diet and  $2.12 \times 10^{-1}$  and  $1.72 \times 10^{-1} \text{ g d}^{-1}$  for cows 309 and 339, respectively, for the halide diet (Table 3). Chloroform ( $\text{CHCl}_3$ ) also showed elevated concentrations as graphed in Figure 6. The emission rates of  $\text{CHCl}_3$  for cows 309 and 339 were  $0.85 \times 10^{-3}$  and  $3.23 \times 10^{-3} \text{ g d}^{-1}$ , respectively, for the regular diet and  $0.283 \times 10^{-3}$  and  $1.52 \times 10^{-3} \text{ g d}^{-1}$  for cows 309 and 339, respectively, for the



**Figure 5.** Measured dimethyl sulfide concentrations in the flow-through chambers for cows 309 and 339 during the experiment with the regular diet. One set of canisters was pressurized (solid square with solid line), and the other set was unpressurized (open slashed square with dotted line). The canisters used to sample the air just before entering the chamber (incoming air, triangle with dotted line) were unpressurized. Arrows represent each time the cow was fed.

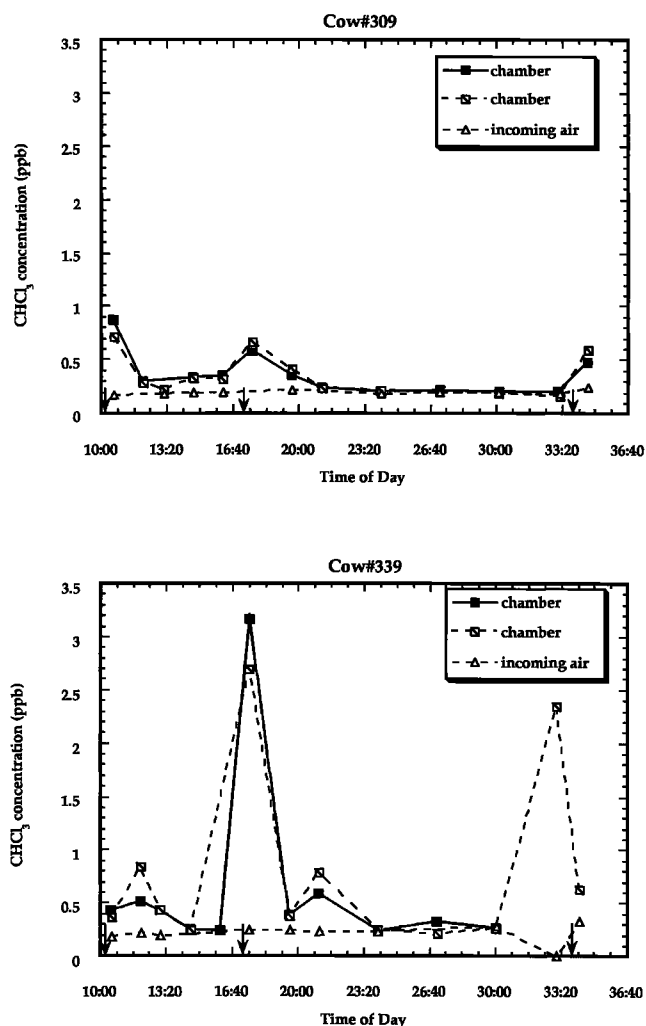
regular diet and  $0.283 \times 10^{-3}$  and  $1.52 \times 10^{-3} \text{ g d}^{-1}$  for cows 309 and 339, respectively, for the halide diet (Table 3). Comparing the results between the regular and halide diet, both cows showed greater emissions of DMS,  $\text{CHCl}_3$ , and  $\text{CH}_3\text{Cl}$  when on the regular diet.

In both experiments with cow 309 we observed elevated concentrations of chloroethane,  $\text{C}_2\text{H}_5\text{Cl}$ , and bromoethane,  $\text{C}_2\text{H}_5\text{Br}$ , but we did not quantify the daily emissions of these compounds. In the June 1997 experiments we did not attempt to measure DMS and chloroform but we did detect and quantify  $\text{C}_2\text{H}_5\text{X}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ). Cow 434 emitted 0.5 mg  $\text{C}_2\text{H}_5\text{Cl}$  and 0.03 mg  $\text{C}_2\text{H}_5\text{Br}$  per day, while cow 956 emitted 0.05 mg  $\text{C}_2\text{H}_5\text{Cl}$  and no  $\text{C}_2\text{H}_5\text{Br}$ ; see Table 4.

The calculated DMS source strength from cattle with the regular diet is  $\sim 110 \text{ Gg yr}^{-1}$ . It is not sensible to speak in terms of a global atmospheric budget of DMS; its atmospheric lifetime is significantly shorter than the time required for transport across the equator, so that one should consider hemispheric scales at most in analyzing its budget. *Andreae* [1990]

has estimated that total global DMS emissions are 19–54 Tg S  $\text{yr}^{-1}$ , with oceanic emissions exceeding those from soils and terrestrial plants by more than a factor of 10. Accordingly, northern hemispheric (where most cattle are) emissions should be  $(3.7\text{--}10) \times 10^{13} \text{ g DMS yr}^{-1}$  or  $\sim 300\text{--}900$  times those from cattle.

A global source strength calculated for  $\text{CHCl}_3$  with the regular diet is 0.403–1.53  $\text{Gg yr}^{-1}$ . *Penkett* [1982] estimated the total anthropogenic source of  $\text{CHCl}_3$  to be 15  $\text{Gg yr}^{-1}$ . *Nightingale et al.* [1995] and *Khalil et al.* [1983] estimated a global oceanic source of 90  $\text{Gg yr}^{-1}$  and 360  $\text{Gg yr}^{-1}$ , respectively. Therefore the global impact of  $\text{CHCl}_3$  from cattle is not significant compared to that of other anthropogenic and oceanic sources of  $\text{CHCl}_3$ . Because atmospheric amounts of  $\text{C}_2\text{H}_5\text{X}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) are not known, it is not clear if emissions from cattle are significant sources for the atmosphere.



**Figure 6.** Chloroform concentrations for cows 309 and 339 during the experiment with the regular diet. One set of canisters was pressurized (solid square with solid line), and the other set was unpressurized (open slashed square with dotted line). The canisters used to sample the air just before entering the chamber (incoming air, triangle with dashed line) were unpressurized. Arrows represent each time the cow was fed.

#### 4. Conclusions

For the field of atmospheric chemistry the most important results of this project are for  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$ . Our results show that emissions from cattle are not a significant source of atmospheric  $\text{CH}_3\text{Br}$ , so that we must continue to seek other sources of about 70–90  $\text{Gg yr}^{-1}$  [Yvon-Lewis and Butler, 1997]. In addition, emissions of  $\text{CH}_3\text{Cl}$  from cattle were not a significant source.

In conclusion, this paper indicates that global emissions of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  from cows are not important sources for the atmosphere and that DMS from cows may be of interest to regional atmospheric chemistry. The emissions of  $\text{CHCl}_3$  and DMS that we detected from cows are probably not of global atmospheric interest, but they may be useful indicators of processes important to those who study animal nutrition and ruminant microbiology and biochemistry. Dimethyl sulfide emitted from cattle may also be of interest to those studying regional atmospheric chemistry near feedlots.

**Acknowledgments.** This project could not have been completed without the assistance of Stanley Tyler (University of California, Irvine), Takehiro Nishida (National Institute of Animal Industry, Tsukuba, Japan), and NSF grants ATM-9321867 and ATM-9731706.

#### References

- Andreae, M. O., Ocean-atmosphere interactions in the global biogeochemical sulfur cycle, *Mar. Chem.*, **30**, 1–29, 1990.
- Andreae, M. O., et al., Methyl halide emissions from savanna fires in southern Africa, *J. Geophys. Res.*, **101**, 23,603–23,613, 1996.
- Atlas, R. M., and R. Bartha, *Microbial Ecology: Fundamentals and Applications*, 560 pp., Addison-Wesley, Reading, Mass., 1981.
- Butler, J. H., The potential role of the ocean in regulating atmospheric  $\text{CH}_3\text{Br}$ , *Geophys. Res. Lett.*, **21**, 185–188, 1994.
- Butler, J. H., and J. M. Rodriguez, Methyl bromide in the atmosphere, *The Methyl Bromide Issue*, edited by C. H. Bell, N. Price, and B. Chakrabarti, John Wiley, New York, 1996.
- Crutzen, P. J., I. Aselmann, and S. Wolfgang, Methane production by domestic animals, wild ruminants, other herbivorous fauna, and humans, *Tellus, Ser. B*, **38**, 271–284, 1986.
- Hungate, R. E., *The Rumen and its Microbes*, 533 pp., Academic, San Diego, Calif., 1966.
- Iwasaki, K., T. Haryu, R. Tano, F. Terada, M. Itoh, and K. Kameoka, New animal metabolism facility especially the description of respiratory apparatus, *Bull. Nat. Inst. Anim. Ind.*, **39**, 41–78, 1982.
- Kabata-Pendias, A., and H. Pendias, *Trace Elements in Soils and Plants*, 2nd ed., CRC Press, Boca Raton, Fla., 1992.
- Khalil, M. A. K., R. A. Rasmussen, and S. D. Hoyt, Atmospheric chloroform ( $\text{CHCl}_3$ ): Ocean-air exchange and global mass balance, *Tellus, Ser. B*, **35**, 226–274, 1983.
- Khalil, M. A. K., R. A. Rasmussen, and R. Gunasardena, Atmospheric methyl bromide-Trends and global mass balance, *J. Geophys. Res.*, **98**, 2887–2896, 1993.
- Kleiber, M., W. M. Regan, and S. W. Mead, Measuring food values for dairy cows, *Hilgardia*, **16**, 511–571, 1945.
- Lobert, M. J., J. H. Butler, S. A. Montzka, L. S. Geller, R. C. Myers, and J. W. Elkins, A net sink for atmospheric  $\text{CH}_3\text{Br}$  in the East Pacific Ocean, *Science*, **267**, 1002–1005, 1995.
- Mass Spectrometry Data Centre, Eight Peak Index of Mass Spectra: Compiled by Mass Spectrometry Data Centre in collaboration with ICI Ltd. (organic division), 2nd ed., Aldermaston, Reading, England, 1974.
- McCraib, G. J., K. T. Berger, T. Magner, C. May, and R. A. Hunter, Inhibiting methane production in Brahman cattle by dietary supplementation with a novel compound and the effects on growth, *Aust. J. Agric. Res.*, **48**, 323–329, 1997.
- Ministry of Agriculture, Forestry and Fisheries, Japanese feeding standard for dairy cattle, Agric., For. and Fish. Res. Council., Tokyo, 1994.
- Moore, R. M., W. Groszko, and S. J. Niven, Ocean-atmosphere exchange of methyl chloride: Results from NW Atlantic and Pacific ocean studies, *J. Geophys. Res.*, **101**, 28,259–28,538, 1996.
- National Research Council (NRC), *Nutrient Requirements of Dairy Cattle*, 6th rev. ed., 157 pp., Nat. Acad., Washington, D. C., 1988.
- Nightingale, P. D., G. Malin, and P. S. Liss, Production of chloroform and other low-molecular-weight halocarbons by some species of macroalgae, *Limnol. Oceanogr.*, **40**, 680–689, 1995.
- Penkett, S. A., Non-methane organics in the remote troposphere, in *Atmospheric Chemistry*, edited by E. D. Goldberg, pp. 329–355, Springer-Verlag, New York, 1982.
- Prather, M. J., M. B. McElroy, S. C. Wofsy, G. Russell, and D. Rind, Chemistry of the global troposphere: Fluorocarbons as tracers of air motion, *J. Geophys. Res.*, **92**, 6579–6613, 1987.
- Prinn, R. G., R. F. Weiss, B. R. Miller, J. Huang, F. N. Alyea, D. M. Cunnold, P. J. Fraser, D. E. Hartley, and P. G. Simmonds, Atmospheric trends and lifetime of  $\text{CH}_3\text{CCl}_3$  and global OH concentrations, *Science*, **269**, 187, 1995.
- Singh, H. B., L. J. Salas, and R. E. Stiles, Methyl halides in and over the eastern Pacific (40°N–32°S), *J. Geophys. Res.*, **88**, 3684–3690, 1983.
- Tait, V. K., R. M. Moore, and R. Tokarczyk, Measurements of methyl chloride in the northwest Atlantic, *J. Geophys. Res.*, **99**, 7821–7833, 1994.
- United Nations, United Nations Statistical Yearbook, 40th issue, 841 pp., New York, 1995.
- Weisenstein, D. K., M. K. W. Ko, and N.-D. Sze, The chlorine budget of the present-day atmosphere: A modeling study, *J. Geophys. Res.*, **97**, 2547–2559, 1992.
- Yuita, K., Iodine, bromine and chlorine contents in the Andosols and in plants of central Honshu, *Soil Sci. Plant Nutr., Tokyo*, **29**, 403–428, 1983.
- Yvon, S. A., and J. H. Butler, An improved estimate of the oceanic lifetime of atmospheric  $\text{CH}_3\text{Br}$ , *Geophys. Res. Lett.*, **23**, 53–56, 1996.
- Yvon-Lewis, S. A., and J. H. Butler, The potential effect of oceanic biological degradation on the lifetime of atmospheric  $\text{CH}_3\text{Br}$ , *Geophys. Res. Lett.*, **24**, 1227–1230, 1997.
- R. J. Cicerone and N.-Y. Wang, Earth System Science, University of California, Irvine, Irvine, CA 92697. (rjccicerone@uci.edu; nywang@uci.edu)
- M. Kurihara and F. Terada, National Institute of Animal Industry, Tsukubashi, Ibaraki-ken 305, Japan. (kurihara@niai.affrc.go.jp; sakura04wnia.affrc.go.jp)
- J. Williams, Department of Environmental and Chemical Science, Chapman University, Orange, CA 92666. (jwilliam@chapman.edu)
- K. Yagi, Environmental Resources Division Japan International Research Center for Agricultural Sciences, 1-2 Ohwashi, Tsukuba, Ibaraki 305-8686, Japan. (kyagi@ss.jircas.affrc.go.jp)

(Received April 21, 1998; November 3, 1998; accepted November 4, 1998.)