Reports

Tropospheric Halogen Gases: Inorganic and Organic Components

Abstract. *Inorganic and organic components of the gaseous tropospheric halogens chlorine, bromine, and iodine have been simultaneously measured. At four diverse remote locations the organic component contained the bulk of the halogen mass, varied less than the inorganic component, and was comparable in concentration to the independently measured halocarbon component.*

Interest in atmospheric halogen gases, particularly those containing chlorine and bromine, has increased dramatically because of concern that halomethanes may affect the stratospheric ozone layer (*1*). A series of gas chromatographic measurements since 1971 indicated that several halomethanes and more complex halogenated hydrocarbons are routinely present at widespread locations in the atmosphere (*2–4*). These studies showed the following halocarbon concentrations [nanograms per standard cubic meter (ng m^{-3} STP)]: Cl, 2200 to 4500; I, 7 to < 30; and Br, < 18. As a result of these findings, considerable attention is now being focused on the organic species of the gaseous atmospheric halogens.

Although there is certainly a significant reservoir of organic halogen gases, the possibility that there is a comparable inorganic halogen reservoir is not excluded by the available data. Several models have been developed for the chemistry of various inorganic halogen species in the troposphere (*5*). In addition, species such as HX and X_2 (X = halogen) were postulated in the older literature to account for the relatively large concentrations of "total" gaseous halogens measured at diverse locations (*6–8*). However, individual inorganic halogen gases have not been identified in the troposphere. Knowledge of the relative sizes of both reservoirs would aid in understanding the overall geochemical cycles of the halogens, and could provide a better perspective for considering perturbations on the global system.

To bridge the gap between the two sets of data for tropospheric halogen gases—the older total data, which include no information about species, and the newer gas-chromatographic data, which quantify certain organic species but not total halogens or any inorganic species—we have developed a technique to separate inorganic from organic gaseous halogens and quantitatively determine their masses. The sampling system consisted of a 0.4-μm Nuclepore filter 47 mm in diameter for particulate collection, followed by one to three 47-mm Whatman No. 41 cellulose filters impregnated with 1.0N LiOH in a 10 percent glycerol-water mixture, followed by five to seven 0.5-g beds of 10- to 12-mesh activated charcoal. Flow rates were 17 to 23 liter min^{-1}. Laboratory tests showed that common inorganic halogen gases such as HX and X_2 were retained with high efficiencies by the impregnated filters, whereas halocarbons such as CCl_4 and CH_3I passed through to the charcoal, where they were collected with high efficiencies. Mean blank values per LiOH filter were Cl, 3.4 μg; Br, 53 ng; and I, 12 ng; blanks per gram of activated charcoal were Cl, 2 μg; Br, $<$ 12 ng, and I, 50 ng. Sample/blank ratios were generally greater than 1 and are listed in Table 1.

Analysis was by nondestructive neutron (n) activation, using the 2-Mw nuclear reactor of the Rhode Island Nuclear Science Center. Samples were irradiated for 2 to 20 minutes at a thermal flux of 4×10^{12} n cm^{-2} sec^{-1}, allowed to decay for 6 minutes, and then counted by using a Ge(Li) detector coupled to a 4096-channel analyzer for 800 seconds live time. Analytical uncertainties were generally 10 to 20 percent.

We report here on field tests at four semiremote to remote sites: Fort Smith, Northwest Territories, Canada; Hays Agricultural Experiment Station, Kansas; Organ Pipe Cactus National Monument, Arizona; and Bermuda. Sample collections were made during June to October 1974 and were 2 to 4 days in duration (the average volume was 100 m^3 STP). The main features of the results are presented in Table 1.

The inorganic gas concentrations showed greater variability than the organic gas concentrations, as shown in

Table 1. Halogen data from the four sampling sites. Inorganic gas was collected on LiOH-impregnated filters. Organic gas was collected on activated charcoal. The number of samples is given in parentheses for each site.

	Arithmetic mean (ng m^{-3} STP)						Total gas/particulate (mass ratio)			Inorganic gas/ total gas (mass %)		
	Inorganic gas			Organic gas								
	Cl	Br	I	Cl	Br	I	Cl	Br	I	Cl	Br	I
Locality												
Arizona (N = 7)	570	11	11	680	17	5	19	8	12	45	38	67
Bermuda (N = 1)	380	24	17	1030	68	28	2.2	7	12	27	26	38
Kansas (N = 3)	170	8	5	1380	39	12	47	4	6	11	17	31
Northwest Territories (N = 5)	80	0.4	0.4	1180	14	3	56	38	15	6	3	13
Analyses of data												
Analytical uncertainty, single sample (%)	10	15	20	15	10	20						
Sample/blank	1–6	0.3–15	1–50	10–20	$>$ 30	2–16						
Geometric mean, all stations	240	5.3	4.3	1040	29	8.1	18	10	11	17	15	32
Geometric standard deviation, all stations	2.4	6.0	5.4	1.4	2.1	2.8	4.4	2.6	1.5	2.5	3.1	2.0

Table 2. Estimated residence times for the various components of the tropospheric halogens.

Halogen	Residence time (days)					
	Particulate		Inorganic gas	Organic gas	Total gas	
	This report	Rahn (*13*)			This report	Literature value (*6–8*)
Chlorine	11	6	21	38	46	30
Bromine	10	7	8	25	24	16
Iodine	14	8	10	18	17	19

Table 1 by comparing geometric mean concentrations at the four locations and the standard deviations of these geometric means. Inorganic gas, expressed as percentage of the total inorganic and organic gas, averaged about 15 percent for Cl, 15 percent for Br, and 30 percent for I. For each halogen the percentage of inorganic gas decreased in the order Arizona > Bermuda > Kansas > Northwest Territories. The same order is observed for the average summer insolation at each site, which suggests that photochemical reactions may play a significant role in organic-inorganic halogen equilibria in the atmosphere. A similar conclusion was reached on theoretical grounds by Zafiriou (*9*), who proposed that much of the atmospheric chemistry of the halogen gases, at least in marine areas, should be photochemically controlled. The concentration of organic halogen gases observed in this study falls in the range of halocarbon concentrations observed previously.

Our data may be used to estimate residence times of organic and inorganic halogen gases and halogens on particles in the lower troposphere. Junge (*10*) showed that the residence times (τ_{res}, years) of a wide variety of atmospheric gases are inversely related to their relative standard deviations of concentration (σ_{rel}) by

$$\tau_{\mathrm{res}}\sigma_{\mathrm{rel}} = 0.14 \text{ year}$$

Using the geometric standard deviations of concentration based on our own and other published data, we have calculated residence times for gaseous and particulate halogens; the results are presented in Table 2. Although annual average concentrations from many points over the entire troposphere should be used for the most precise calculations, our data can at least suggest approximate relative residence times. When data from only this study are considered, residence times vary in the following order: for Cl, particulate < inorganic gas < organic gas < total gas; for Br and I, particulate ≈ inorganic gas < organic gas ≈ total gas. Residence times calculated from independent larger sets of data, which were available for particulate and total gaseous halogens, were generally somewhat shorter than those calculated from our data only.

The calculated residence times are reasonable in several respects: (i) the particulate residence times of a few days agree with current estimates for aerosols obtained by other means (*11*); (ii) the generally longer residence times of the gases than of the particulates agree with the general trend of atmospheric trace gases compared to particulates and with the specific findings of Moyers and Duce (*7*) for Br at Hawaii and of Duce *et al.* (*8*) for Br and I in Antarctica; (iii) the charcoal-captured organic halogens should be less reactive (longer-lived) than the hydroxide-captured inorganic halogens; and (iv) the total gaseous halogens, being a mixture of inorganic and organic components, should have calculated residence times between those of their two components if the components are independent or longer than the residence time of either component if one is the precursor of the other. The data in Table 2 suggest that either organic or inorganic Cl is the precursor of the other, but this appears not to be the case for I and Br.

Data from all compilations indicate that gaseous Cl in all forms has a significantly longer residence time than either Br or I. This agrees qualitatively with what one would expect for Cl and I if CH_3Cl and CH_3I were the principal gaseous tropospheric species (*3, 4*) because CH_3I is rapidly photolyzed whereas CH_3Cl is not (*9, 12*). For both determinations of particulate residence time, I has the largest values. This is in accord with a recent compilation (*13*), which shows particulate I to have a typical mass-median diameter of 0.6 μm, smaller than either Br (0.9 μm) or Cl (0.6 to 5 μm).

In summary, Cl, Br, and I are predominantly organically bound in the gas phase in the lower troposphere at all four locations investigated to date. Approximately 85 percent of the Cl and Br and 70 percent of the I appear to be organically associated. Thus, anthropogenic perturbations of the organic gaseous halogen component, such as the buildup of Freons, constitute nearly equivalent perturbations of the total gaseous halogen reservoir. The percentage of organic gas for each halogen decreases with increasing solar radiation, suggesting that photochemical interactions play a significant role in their atmospheric chemistry. Calculated atmospheric residence times are 1 to 2 weeks for particulate and inorganic gaseous components and 2 to 6 weeks for the organic gaseous components. Gaseous Cl has a longer residence time than gaseous I or Br.

KENNETH A. RAHN
RANDOLPH D. BORYS
ROBERT A. DUCE

Graduate School of Oceanography,
University of Rhode Island,
Kingston 02881

References and Notes

M. J. Molina and F. S. Rowland, *Nature (London)* **249**, 810 (1974); R. J. Cicerone, R. S. Stolarski, S. Walters, *Science* **185**, 1165 (1974).

2. C.-W. Su and E. D. Goldberg, *Nature (London)* **245**, 27 (1973); P. E. Wilkniss, J. W. Swinnerton, D. J. Bressan, R. A. Lamontagne, R. E. Larson, *J. Atmos. Sci.* **32**, 158 (1975).
3. E. P. Grimsrud and R. A. Rasmussen, *Atmos. Environ.* **9**, 1014 (1975).
4. J. E. Lovelock, R. J. Maggs, R. J. Wade, *Nature (London)* **241**, 193 (1973).

S. C. Wofsy, M. B. McElroy, Y. L. Yung, *Geophys. Res. Lett.* **2**, 215 (1975); D. H. Stedman, W. L. Chameides, R. J. Cicerone, *ibid.*, p. 333.

6. C. E. Junge, *Tellus* **8**, 127 (1956); *ibid.* **9**, 528 (1957); R. Chesselet, J. Morelli, P. Buat-Menard, *Nobel Symposium 20: The Changing Chemistry of the Oceans* (Wiley, New York, 1972), p. 93; R. A. Duce, J. W. Winchester, T. W. Van Nahl, *J. Geophys. Res.* **70**, 1775 (1965); J. L. Moyers, W. H. Zoller, R. A. Duce, *J. Atmos. Sci.* **28**, 95 (1971); ———, G. L. Hoffman, *Environ. Sci. Technol.* **6**, 68 (1972); J. L. Moyers and R. A. Duce, *J. Geophys. Res.* **77**, 5229 (1972).
7. J. L. Moyers and R. A. Duce, *J. Geophys. Res.* **77**, 5330 (1972).
8. R. A. Duce, W. H. Zoller, J. L. Moyers, *ibid.* **78**, 7802 (1973).
9. O. C. Zafiriou, *ibid* **79**, 2730 (1974).
10. C. E. Junge, *Tellus* **26**, 477 (1974). Junge used primarily the relative standard deviation (coefficient of variation), defined for a variable x by $\sigma_{\mathrm{rel}} = \sigma_x \bar{x}_{\mathrm{a}}$, where $\bar{x}_{\mathrm{a}}$ is the arithmetic mean of x. For atmospheric gases with large σ_{rel}, it becomes physically more reasonable to express their variation by the geometric standard deviation, defined as $\sigma_{\mathrm{g}} = \exp \sigma_{\ln x}$. The geometric standard deviation is a multiplicative factor; that is, for a log-normal distribution 68.3 percent of the population is found within a factor $\pm\, \sigma_{\mathrm{g}}$ of the geometric mean. Although σ_{g} and σ_{rel} are respectively multiplicative and additive, as they become smaller they approach the same numerical value and can be used interchangeably. We prefer to use the more universal σ_{g} in residence-time calculations.
11. N. A. Esmen and M. Corn, *Atmos. Environ.* **5**, 571 (1971); C. E. Junge, *J. Geophys. Res.* **77**, 5183 (1972).
12. O. C. Zafiriou, *J. Mar. Res.* **33**, 75 (1975).
13. K. A. Rahn, *Extern* **4**, 286 (1975).
14. Supported by NSF grants GA-31918 and GX-33777. The samples were analyzed with facilities of the Rhode Island Nuclear Science Center. We thank L. Vance of the Northern Canada Power Commission, W. Baxter of the Fort Hayes Agricultural Experiment Station, E. Rodriguez and R. Thomas of Organ Pipe Cactus National Monument, and W. Sterrer of the Bermuda Biological Station for making their facilities available, and J. Moyers of the University of Arizona for valuable discussions and aid in the development of the collection and sampling program.

2 December 1975; revised 3 February 1976