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Estimation of global vehicular methyl bromide emissions: Extrapolation from a case study in Santiago, Chile

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Abstract. Between June 1 and June 8, 1996, 144 whole air samples were collected in Santiago, Chile. The temporal and geographical enhancement of CH_3Br correlated with incomplete combustion tracers emitted from vehicles during the morning commute. From these, a city-wide CH_3Br/CO volume emission ratio of 2.2×10^{-6} was measured in ambient air. Without using the CO measurements, we estimate an annual release of 8.9 tons of CH_3Br in Santiago based solely upon enhanced concentrations observed throughout the study area during the morning traffic period. This enhancement corresponds to 8.0×10^{-6} kg CH_3Br emitted for each liter of gasoline used (leaded and unleaded). By scaling the annual gasoline usage in Santiago to countries still using leaded gasoline, and assuming the above 8.0×10^{-6} kg/L value holds true, a global vehicular CH_3Br emission of 4 ± 3 Gg/year is calculated. This small vehicular CH_3Br emission source strength will not improve the current CH_3Br budget imbalance.

Introduction

Methyl bromide (CH_3Br) has a global tropospheric average concentration of 9.5 ± 0.5 pptv and an atmospheric lifetime of approximately 0.7-0.8 year [Yvon-Lewis and Butler, 1997; Colman *et al.*, 1998; Wingenter, 1998]. Methyl bromide accounts for 50 to 60% of the total organic bromine that enters stratosphere [Wamsley *et al.*, 1998]. Once these organobromine compounds are photolyzed in the stratosphere, the released bromine atom participates in ozone destroying cycles. Bromine compounds are estimated to contribute up to 25% of stratospheric ozone destruction in springtime polar regions [McElroy *et al.*, 1986; Anderson *et al.*, 1989; Poulet *et al.*, 1992].

The most recent global CH_3Br source strength estimate is 122 Gg/yr, while sinks are estimated at 205 Gg/yr [Butler and Yung, SOS1997]. This indicates that the CH_3Br budget is not well understood. One area of uncertainty is emissions from vehicular exhaust. Few vehicles were used in previous studies and a wide range of emissions was reported. Using a 1974 Opel Kadett C operating in neutral gear, Baumann and Heumann's [1987] results suggested the CH_3Br mass emission factor (BHEF) was 23% (15-28%) of emitted bromine. Using a 1972 Ford LTD and a 1973 Dodge Dart, Hao [1986] reported a CH_3Br mass emission factor of $0.12 \pm 0.11\%$. Using the same BHEF value, Speigelstein estimated 15 Gg/yr (8.6-22) of CH_3Br emissions in 1991, but an U.S.E.P.A. study estimated 0.5-1.5 Gg/yr for 1992 [Penkett, *et al.*, 1995]. From the worldwide bromine content in leaded gasoline (23 ± 2.5 Gg/yr in 1995) and again the BHEF value, Thomas *et al.* [1997] estimated 5.7 ± 1.7 Gg/yr was emitted in 1995. From 12 samples collected along busy roads in Norwich, Middlesbrough and Newcastle (UK), Baker *et al.* [1998] reported annual emissions of 1.5 Gg for 1995, and a range of 1-3 Gg/yr.

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Experimental

In this paper global CH_3Br emissions are estimated based on whole air samples collected throughout Santiago, Chile. Santiago has a population of 5 million people and 735,000 vehicles, 673,000 of which are passenger cars [INE, 1995]. The city is situated in a basin at an average altitude of 520 m. The coastal ranges are to the west and Andes mountains to the east of the city. The Mapocho and Maipo river valleys cut through the coastal ranges to the northwest and southwest.

Between June 1 and June 8, 1996, 144 whole air samples were collected in evacuated 2-liter stainless steel canisters in Santiago. A study region of 25.0 x 21.4km (70° 31.8'– 70° 47.4' W and 33° 21.6' – 33° 32.7' S) was divided into a 7 x 6 grid (Figure 1), covering most of metropolitan Santiago. With the collaboration of 30 Pontificia Universidad Catolica de Chile (PUC) students and faculty members, forty-five samples were collected at approximately 5 a.m. on June 4 at the grid locations noted in Figure 1. Minimal vehicular activity was observed before 5:30 a.m.; however, several samples were collected around 6 a.m., after the morning bus service started. An additional 43 samples were collected at the same locations at 9 a.m., after morning traffic activities were fully developed. A comparison of the two grid results represents the effects of meteorological transport and emissions.

Two samples were also collected inside and another sample outside the 2 km long Zapata tunnel to estimate the collective CH_3Br emissions of the many types of vehicles traveling in the tunnel. Moderate to heavy traffic of passenger vehicles (roughly 2/3 of total) and large freight trucks were observed moving at approximately 40 km/hr.

Observations of surface wind direction and strength were made at most of the sampling locations. In general, the study area had very weak wind (< 0.8 m/s) and stable atmospheric conditions. The non-SI unit of degree/hr is used in Figure 1 to illustrate that movement of air parcels during the study period is almost entirely within the study area.

The samples were returned to our UC Irvine laboratory for gas chromatographic analysis of methane, CO, 72 nonmethane hydrocarbons (NMHCs), 28 halocarbons and 5 alkyl nitrates. Detailed analytical descriptions are given in Hurst [1990] and Blake *et al.* [1996].

Results and Discussion

Evidence of Methyl Bromide Release in Vehicular Exhaust

The 5 a.m. and 9 a.m. median values of carbon monoxide (CO), ethyne, iso-pentane, ethylene dibromide, (EDB), and CH_3Br are given in Table 1. The calculation for CH_3Br to CO emission ratio is illustrated in Figure 2, and will be discussed in

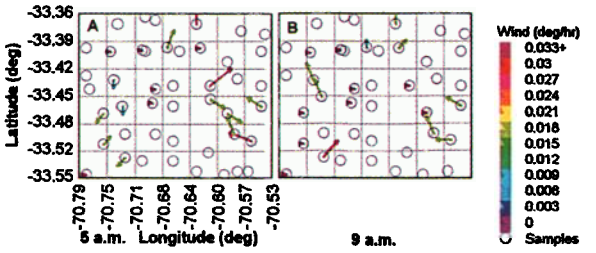

Figure 1. Sampling locations and wind vectors on June 4 at 5 a.m. and 9 a.m. (A and B). Wind strength (in degree/hour, 1 m/s = 0.04 degree/hour or approximately one division in this figure) is represented by both the color and the length of the arrows. Zero wind strength is represented by east facing purple triangles.

detail later. Both CO and ethyne are good tracers for incomplete combustion. Iso-pentane is the largest vapor phase component in gasoline and diesel. The large enhancement of CO and ethyne at 9 a.m. suggests significant fossil fuel combustion. The increased levels of i-pentane and EDB (a leaded gasoline additive) indicate a large increase in vapor emissions of petroleum fuel. A 12 pptv increase in median CH_3Br values was observed between 5 and 9 a.m. (Table 1), indicating a CH_3Br source associated with morning activities. However, the 5 a.m. CH_3Br median value of 29 pptv was significantly higher than the 9.3 pptv upwind value observed at the nearby Chilean coast (enhanced compared to similar latitude concentrations), suggesting that CH_3Br has additional sources not associated with morning activities.

Concentration matrixes for CO, ethyne, i-pentane, EDB and CH_3Br are constructed using Stanford Graphics' inverse distance square method. The results of these 7 x 6 matrices are displayed in Figures 3-5 as 3-D color contours. Concentration levels observed are plotted in the Z-axis and color-coded. The mixing ratios of gases observed at 5 a.m. were generally much lower than those at 9 a.m., consistent with the observation of lower early morning vehicular activity.

The elevated concentrations observed at 9 a.m. are most prominent along a northeast to southwest direction across Santiago. This enhanced concentration pattern falls on the major traffic routes and clearly illustrates the impact of motor vehicle usage during the morning commute. The calm and stable atmospheric conditions contributed to maintain the chemical distribution of tracers near their local sources.

Both the 5 a.m. and 9 a.m. CH_3Br concentration profiles (Fig. 5, A and B) are clearly different than the other gases. Very high levels of CH_3Br were observed in the rural farming area in the northwest communities of Quilicura, Renca and Pudahuel. The

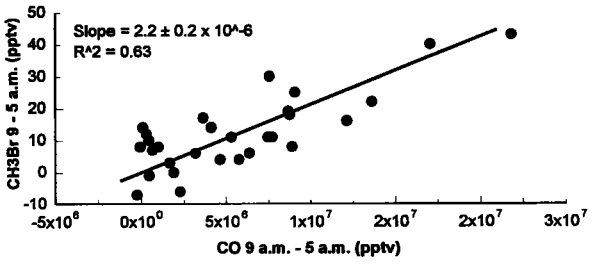

Figure 2. The changes in CH_3Br levels between 5 a.m. and 9 a.m., observed at 29 locations throughout Santiago, are correlated to those of CO. The influence of a terrestrial CH3Br source contributed to the larger scattering observed at lower CO levels.

Table 1. Median Mixing Ratios in pptv for Selected Trace Gases

	CO (ppbv)	Ethyne	i-Pentane	EDB	CH_3Br
5 a.m.	1872	14158	9281	1.91	29
9 a.m.	5391	50998	19199	4.24	41
9 a.m. – 5 a.m.	3519	36840	9918	2.33	12
% increase	188%	260%	107%	122%	40%
Emission ratio to CO		7.7×10^{-3}	3.4×10^{-3}	6.2×10^{-7}	2.2×10^{-6} *
Standard error		0.6×10^{-3}	0.5×10^{-3}	0.5×10^{-7}	0.5×10^{-6} *
R^2		0.78	0.54	0.76	0.37*

* Thirteen samples collected near local CH_3Br or CO sources were removed from the data set for the emission ratio calculation.

land in that area had been plowed but not planted. Because CH_3Br concentration levels in this farm region were very high at 5 a.m., there was most likely a continuous terrestrial source of CH_3Br in that region. The presence of elevated CH_3Br at 9 a.m. throughout a 10 x 10 km area suggests a regional rather than a point source. The strength and possible identity of this unknown source will be investigated in future studies.

For each of the 42 grid locations, the 5 a.m. CH_3Br concentration was subtracted from the 9 a.m. value. The difference (Fig. 5C) reveals the same morning commute pattern as seen in CO and ethyne (Fig. 3). The difference in CH_3Br concentrations (9 a.m. – 5 a.m.) was correlated to the same changes in CO levels (Table 1 and Fig. 2), and a CH_3Br to CO volume emission ratio of $2.2 \pm 0.2 \times 10^{-6}$ was calculated. Thirteen locations were removed from the CH_3Br to CO slope calculation because they were near local CH_3Br or CO sources. The presence of a large terrestrial CH3Br source contributed to an increase in scatter, especially for samples with CO levels less than 5000 ppbv. This scatter is reflected in the somewhat low R^2 value of 0.63. Also given in Table 1 are the emission ratios of ethyne, i-pentane and EDB relative to CO, standard error of the ratios and the R^2 values, but those values were calculated using all 42 locations.

The difference of concentration levels observed inside and outside the Zapata tunnel yielded a CH_3Br/CO enhancement ratio of 4×10^{-6} (two samples yielding 3.9 and 4.2×10^{-6} respectively), in reasonably good agreement with the emission ratio observed at 38 locations throughout Santiago. Because CO is also emitted by combustion of fuels other than petroleum (e.g. LPG), the lower Santiago CH_3Br/CO emission ratio is expected. In addition, because traffic in the Zapata tunnel did not experience the same congestion as that in Santiago, we feel the 2.2×10^{-6} Santiago emission ratio better represents the different driving scenarios in a large metropolitan area. A CH_3Br/CO ratio of 2.66×10^{-6} was reported by Baker *et al.* [1998] for UK roadside samples. This excellent agreement suggests the CH_3Br/CO vehicular emission ratios may be similar for many regions in the world.

Similar observations of CH_3Br/CO emission ratio over different regions are probable for two reasons: first, there are many CO sources that do not release CH_3Br, but are emitted in close proximity to vehicular usage, e.g., incomplete combustion of LPG. Second, CH_3Br to lead content emission factors are highly uncertain because of the few vehicles used in laboratory studies. As reviewed by Thomas et al. [1997], emissions of CH_3Br from leaded gasoline in the few laboratory studies range over two orders of magnitude. Even though the maximum lead content in the European Community is only 0.15 g/L whereas the Latin America and the Caribbean leaded gasoline range between 0.2 to 0.77 g/L [World Bank, 1996], actual driving conditions and

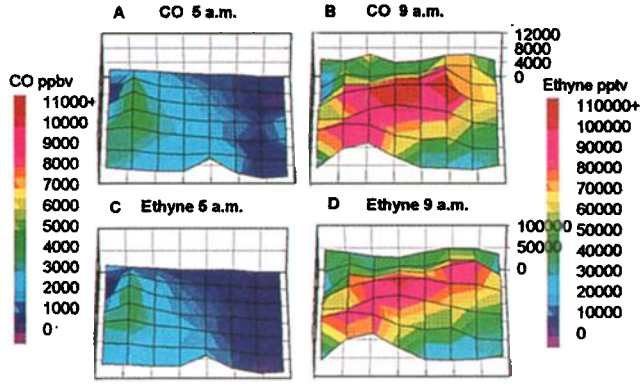

Figure 3. Concentration color contours of carbon monoxide (CO) (A and B) and ethyne at 5 a.m. and 9 a.m. (C and D). The color code and the Z-axis represent concentration levels. Carbon monoxide and ethyne are good tracers for incomplete combustion. Both compounds are strongly enhanced by the morning commute.

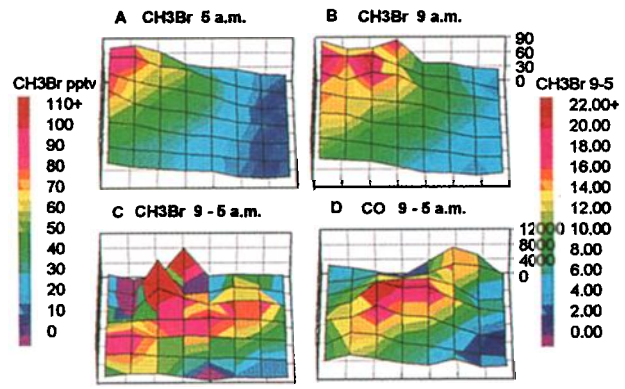

Figure 5. (A and B) Concentration color contours of CH_3Br at 5 a.m. and 9 a.m. The difference between the two periods reveals enhancement patterns associated with morning commute (C), color scale is from 0 to 22 pptv. (D) is the difference in CO between the 5 a.m. and 9 a.m. samplings, with the same color scale used in Figures (3.A) and (3.B).

vehicular compositions probably have the most direct impact on CH_3Br emissions.

Because each of the 7 x 6 grid cells represents an area of 3.57 x 3.57 km and normally only one sample was collected per grid cell, the features of the 3-D contour will shift depending on wind direction and strength. This is most likely the cause of the large deficit and surplus of differential CH_3Br observed in the northwest rural region (Fig. 5C). A z-axis concentration scale of 0-100 pptv was used in Figure 5C because of this surplus. However, the morning traffic enhancement pattern is well illustrated by the 0-22 pptv color scale.

Estimation of Santiago Vehicular Methyl Bromide Emissions and Emission Ratios

The emission budget of a compound can be estimated by taking the differences in concentration at two time periods, multiplied by the volume of air affected. The previously discussed CH_3Br median value increased by 12 pptv between 5 a.m. and 9 a.m. The study area is 25.0 x 21.4 km. The boundary layer height of approximately 200 ± 100m at 9 a.m. was visually estimated. A "box" of air above Santiago with a volume of 1 x 10^{14} liters is assumed. The 43 surface wind observations gave a median wind strength of 0.3 m/s (or 1.1 km/hr, with an estimated range of 0-2 km/hr). This estimate agrees well with observations from the Chilean CONAMA monitoring stations and supports a one day ventilation of the study volume.

An enhancement of 12 pptv CH_3Br in this partially ventilated 1 x 10^{14} liter "box" corresponds to 6.1 kg of CH_3Br released in Santiago between 5 a.m. and 9 a.m. The uncertainty in boundary layer height and wind speed places the upper and lower limit at 10.3 and 2.6 kg/4hrs, respectively. In addition to the 1 x 10^{14} liter box calculation which extends over the entire study area, a smaller area partial "box" calculation was made for the traffic corridor only. The calculated traffic corridor CH_3Br emission budget yields the same result. This suggests that the 12 pptv CH_3Br increase used in the box calculation is consistent with the morning traffic emissions. Similarly heavy traffic and congestion were observed throughout the city from 6 a.m. to 10 p.m. during our three visits in August 1995, June and again in November 1996. If we assume CH_3Br is released during the high traffic hours only (6 a.m. to 10 p.m.) and the release rate remain constant throughout the year, an annual Santiago vehicular CH_3Br release rate of 8.9 (-5, +6) x 10^3 kg is calculated.

In 1995, Santiago used 3.92 x 10^8 liters of unleaded and 7.16 x 10^8 liters of leaded gasoline (0.31 g Pb/liter, [World Bank, 1996], for a total of 1.11 x 10^9 liters [SEC, 1995]. This corresponds to a CH_3Br to gasoline (both leaded and unleaded) emission ratio of 8.0 x 10^{-6} kg/L. If it's assumed that CH_3Br is only emitted from vehicles that use leaded gasoline, then the CH_3Br/leaded gasoline ratio is 1.2 x 10^{-5} kg/L, or 0.040 g of CH_3Br emitted per gram of lead. In 1995, Santiago consumed 89 tons of bromine in leaded gasoline (Br:Pb weight ratio of 0.4), suggesting a CH_3Br to bromine mass emission factor of 10% (4-17%). This Santiago emission factor is lower than the BHEF value of 23% (15-28%) and perhaps more representative of urban situations.

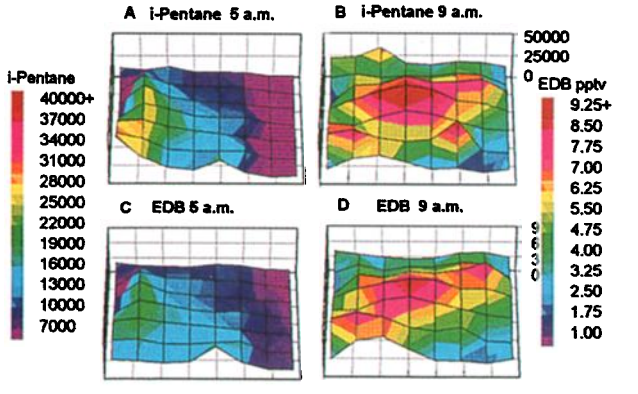

Figure 4. Concentration color contours of iso-pentane (A and B) and ethylene dibromide (EDB) at 5 a.m. and 9 a.m. (C and D). Iso-pentane is the largest vapor phase component of gasoline and diesel. Ethylene dibromide is a leaded gasoline additive. The enhancement of these gases suggests petroleum fuel was emitted during the morning hours.

Estimation of Global Vehicular Methyl Bromide Emissions

In 1995, 1.06 x 10^{12} liters of gasoline were used globally. Nine unleaded-only countries (United States, Japan, Canada, Germany, Brazil, South Korea, Sweden, Colombia and Austria) consumed 5.93x10^{11} liters of unleaded gasoline, or 56% of world

gasoline consumption [Thomas, 1995 and UN, 1997]. Assuming the Santiago CH_3Br/gasoline emission ratio is similar for all other countries still using leaded gasoline, we estimate global vehicular emissions are 4 ± 3 Gg/year.

An alternative method is to extrapolate by lead usage in gasoline. The 7.16×10^8 liters of Santiago leaded gasoline contained 2.2×10^5 kg of lead. Thomas et al. [1997] estimated 5.0×10^7 kg of lead used in gasoline worldwide in 1995. This implies a global CH_3Br emissions of 2.0 (0.8-3.4) Gg/yr, within the lower range of the 4 ± 3 estimate. Given the variability in global vehicular composition, traffic conditions, emission factors and other uncertainties, 4 ± 3 Gg/year is likely a better estimate.

Conclusions

Grid sampling during different times of day demonstrates the atmospheric impact of vehicular usage during the morning commute. In Santiago, methyl bromide emissions are associated with vehicular exhaust, but also have a significant and apparently continuously emitting unidentified source. The city-wide CH_3Br to CO volume emission ratio for Santiago is 2.2×10^{-6}. Approximately 8.0×10^{-6} kg of CH_3Br is released per liter of gasoline used in Santiago and likely other cities that still use leaded gasoline. Assuming the Santiago CH_3Br to gasoline usage ratio is representative of countries still using leaded gasoline, a global vehicular CH_3Br emission of 4 ± 3 Gg/year is estimated. Results from this study suggest the vehicular CH_3Br source strength is several times less than the upper limit reported previously and will not narrow the gap between CH_3Br sources and sinks.

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