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## Bromine emissions from leaded gasoline

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**Abstract.** Gasoline lead additives contain brominated compounds. When leaded gasoline is combusted, some of the bromine can be emitted as methyl bromide which can contribute to stratospheric ozone depletion. Based on world use of lead in gasoline and on gasoline scavenger formulations, we estimate that worldwide use of bromine in gasoline peaked in the early 1970s at  $170 \pm 20$  kT/yr and that by 1995 this had decreased to  $23 \pm 2.5$  kT/yr. The fraction of bromine in leaded gasoline that is emitted as methyl bromide ranges over two orders of magnitude. At the upper end of this range, the decrease in methyl bromide emissions from the 1970s to the 1990s could have equaled the increase in emissions from use of methyl bromide as a fumigant in the same period.

### Introduction

Methyl bromide,  $\text{CH}_3\text{Br}$ , is the most abundant organobromine gas in the atmosphere; typical concentrations are 11.1 and 8.5 ppt in the northern and southern hemispheres, respectively [Lobert *et al.*, 1995]. Although most methyl bromide released at the surface is destroyed by tropospheric OH, some  $\text{CH}_3\text{Br}$  enters the stratosphere. Stratospheric ozone destruction by inorganic bromine compounds has been demonstrated [Anderson *et al.*, 1989] but the fraction of this bromine due to anthropogenic  $\text{CH}_3\text{Br}$  and synthetic halon compounds compared to that from natural  $\text{CH}_3\text{Br}$  is not completely clear.

The budget of atmospheric  $\text{CH}_3\text{Br}$  is not well established. A useful, though approximate, 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, i.e.,

$$\text{Sources} = \text{Sinks} = B/T_r \quad (1)$$

The most reliable quantity in (1) is the atmospheric burden: 145 kT of  $\text{CH}_3\text{Br}$  (data are from Butler [1994] and Khalil *et al.* [1993] and are probably accurate to within 15%). No clear temporal trend has been observed; Khalil *et al.* [1993] found an increase of  $0.15 \pm 0.1$  ppt/yr from measurements taken between 1983 and 1992. Current information implies that  $T_r$  is about 0.8 years [Butler and Rodriguez, 1996; Shorter *et al.*,

1995]. If true, global sources must be about 180 kT/yr in steady state.

Independent estimates of  $\text{CH}_3\text{Br}$  sources can be obtained by studying the sources themselves or by estimating sinks; Butler and Rodriguez [1996] estimate that there may be an unidentified (predominantly northern) source of  $\text{CH}_3\text{Br}$  of about 40 kT/yr. Alternatively, current sink estimates may be too large; for discussion of individual sources and sinks, see Yvon and Butler [1996], Butler and Rodriguez [1996], and Shorter *et al.* [1995]. Briefly, major sources are thought to be about 20 kT/yr from biomass burning [Andreae *et al.*, 1996] and 20 to 60 kT/yr from fumigation of agricultural soils and of harvested crops [Penkett *et al.*, 1995]. Emissions from non-agricultural applications may be only 6 kT/yr [Penkett *et al.*, 1995]. The burning of leaded gasoline is a highly uncertain source, 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].

Thus, at present we have unsatisfactory understanding of the sources and possibly the sinks of  $\text{CH}_3\text{Br}$  and its identified sources do not appear to be enough to explain its atmospheric amounts. Accordingly, it is desirable to quantify the possible source of  $\text{CH}_3\text{Br}$  from the combustion of leaded gasoline. It may also be important to quantify the history of this possible source because of the conceivable circumstance that the temporal growth of the release from agricultural fumigations has been matched by a temporal decrease in the amount released from leaded gasoline usage. Further, one wishes to know the relative amounts of  $\text{CH}_3\text{Br}$  released north and south of the equator so that any putative source budget may be modeled against the constraint that the average north/south ratio is 1.3 [Lobert *et al.*, 1995].

Leaded gasoline additives contain brominated and chlorinated compounds which act as scavengers to prevent lead from depositing in the engine, and methyl bromide has been measured in the emissions of automobiles using leaded gasoline. Spiegelstein estimated a global methyl bromide emission of about 15 kT/yr for 1991-92, and W. Thomas estimated an emission of 0.5 to 1.5 kT/yr for 1992 [Penkett *et al.*, 1995]. These results differed due to their estimates of the amount of bromine used in gasoline worldwide. Below we use data on the amount of lead that has been used in gasoline, and on the bromine content of lead additive formulations, to estimate the use of bromine in gasoline worldwide.

### World Use of Lead in Gasoline

Although the use of leaded motor gasoline has been eliminated in the U.S. and a few other countries, it is still used

in most countries. As shown in Figure 1, annual world use of lead in gasoline peaked in the early 1970s at almost 400 kT/yr. Growing appreciation of the health consequences of lead exposure, and the introduction of catalytic converters (which require unleaded gasoline for proper operation) has led to reduced use of leaded gasoline worldwide [Thomas, 1995]. By 1995 world use of lead in gasoline had fallen to about 50 kT/yr. Total world production of lead in gasoline additives from 1930 to the 1990s was about 9500 kT; the U.S. consumed about two-thirds of this, 6500 kT. Southern hemisphere consumption averaged 20 kT/yr through the 1970s and most of the 1980s, and fell to about 9.5 kT/yr by 1995. Northern hemisphere consumption was 95% of the total in 1970, and remained about 80% of the total in 1995. Figure 1 also shows U.S. production data from 1968; these data will be used later with regard to the bromine content of these additives.

### World Use of Bromine in Gasoline

The production of lead additives in gasoline has been dominated by a small number of companies (Dupont, Ethyl, and Octel) and standardization of additive formulations occurred during World War II (B. Maxwell, Ethyl, personal communication, 1996). As of the mid-1990s, Octel, owned by Great Lakes Chemical, produces more than 95% of the world's gasoline lead additives. The only other remaining manufacturers are two small plants, in Russia and Germany.

The first leaded gasoline, sold in February, 1923, contained 7 g triethylbromide and 1.5 g carbon tetrachloride per gallon of gasoline as scavengers. In March of 1923, the formulation was changed to 3 parts tetraethyl lead (TEL) and 2 parts carbon tetrachloride. In September of 1923, trichloroethylene was substituted for the carbon tetrachloride (A. Loeb, unpublished manuscript, 1994).

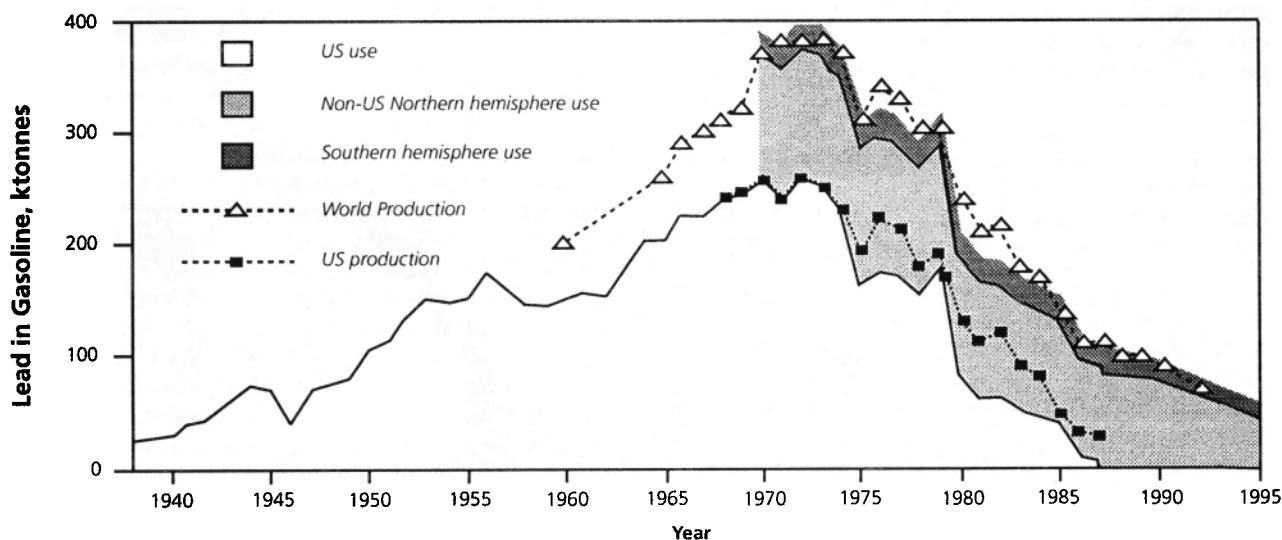
In 1925, the formulation was changed to 35.7% ethylene dibromide ( $C_2H_4Br_2$  or EDB), 61.4% TEL, and 2.9% chlornaphthalene (weight percents) [Randi, 1952]. This mixture has a Pb:Br atom ratio of 1:2 and a Br:Pb weight ratio of 0.8, and is what is now called "aviation fluid". Beginning

in the 1940s, part of the EDB was replaced with ethylene dichloride (EDC), as a cost saving measure, in the gasoline additive mixture used for automobiles. This "motor fluid" mixture has a Pb:Cl:Br atom ratio of 1:2:1 (and thus a Br:Pb weight ratio of 0.4) and contains 61.48% TEL, 17.8% EDB, 18.8% EDC, and 1.92% dye [Otto and Montriuil, 1976]. This has been the primary lead additive fluid sold worldwide (Personal communications, B. Maxwell, Ethyl, and J. Caldwell, U.S. EPA, 1996). Tetramethyl lead is also used to make a similar "motor fluid" formulation [O'Connor et al., 1977].

The fully brominated mixture, "aviation fluid", continued to be used for aviation gasoline. Much less aviation gasoline is used than motor gasoline. For example, in the U.S., consumption of aviation gasoline is about 0.25% of the consumption of motor gasoline [U.S. Dept. of Energy, 1991], and some small airplanes are now certified to use unleaded motor gasoline (S. Henry, Great Lakes Chemical, personal communication, 1996). The lead content of aviation gasoline is typically 0.6 g/L (J. Caldwell, U.S. EPA, and B. Maxwell, Ethyl, personal communications, 1996).

"Aviation fluid" has been used for motor gasoline in some countries. One such country is the Soviet Union, which has typically produced about half of its requirement for lead additives, and imported the rest (D. Gidlow, Octel, personal communication, 1995, and B. Maxwell, Ethyl, personal communication, 1996). Its own production has a reported formulation similar to standard aviation fluid: 55% TEL, 34% dibromopropane, and 5% chloronaphthalene. During the 1970s and 1980s, the Soviet Union is estimated to have used about 15 kT/yr of lead in gasoline, which it reduced to about 9 kT/yr as of 1995 (Russian Ministry of Fuel and Energy, unpublished data, 1995). In addition, Australia used a mixture of aviation fluid and tetramethyl-lead motor mix. The average Br:Pb ratio in Australian gasolines has been estimated to be 0.61 [O'Connor et al., 1977].

At least one country — Germany — does not use scavengers in its leaded gasoline. The use of halogenated scavengers has been banned in Germany since 1992, due to the potential for



**Figure 1.** A fifty-year view of global production and consumption of lead in gasoline. For consumption, global use is disaggregated into three parts of the world: the U.S., the rest of the northern hemisphere, and the southern hemisphere. Primary sources are ILZSG [1992], Grandjean and Nielson [1979], Nriagu [1990], Octel [1970-1995], Socolow and Thomas [1997], and Thomas [1995].

emission of halogenated compounds, such as dioxin, as well as the corrosive effects of scavengers on engine parts. Studies undertaken in cooperation with the German petroleum and automobile industries found no adverse effects from the elimination of scavengers from gasoline with up to 0.15 g/L lead, which is the maximum lead content in the European Community and many other countries [Schmauder, 1990].

Data on total EDB consumption can provide additional constraints on bromine use in gasoline. While worldwide data are not available, data are available on U.S. EDB use. For the years 1968 to 1984, the average Br:Pb ratio in U.S. EDB consumption versus U.S. gasoline lead additive production was 0.46 [Roskill, 1992; Klingman, 1975]. This provides an upper bound on the bromine content of U.S.-produced gasoline additives, since a small amount of EDB was used as a fumigant. As Figure 1 shows, U.S. lead additive production accounted for more than two-thirds of worldwide production until the 1980s. For the non-U.S. produced lead additive, we take the 0.6 Br:Pb ratio of Australian gasoline as an upper bound. In this case, the weighted average upper bound Br:Pb ratio of total worldwide gasoline lead additive production is about 0.5.

Based on this upper estimate, and the typical ratio of 0.4 for U.S. and European gasolines, our best estimate of the world average Br:Pb ratio is  $0.45 \pm 0.05$ . As Figure 2 shows, this implies that annual world use of bromine in gasoline peaked in the early 1970s at about  $170 \pm 20$  kT, was  $100 \pm 11$  in 1980,  $65 \pm 7$  in 1985,  $40 \pm 5$  kT in 1990,  $30 \pm 3.3$  kT in 1992-3, and  $23 \pm 2.5$  kT in 1995. Southern hemisphere use was a relatively constant  $9 \pm 1$  kT/yr from 1970 to 1985, and dropped to about  $6.6 \pm 0.7$  kT/yr by 1990 and about 4.3 kT/yr by 1995. The north/south ratio of bromine used in gasoline was  $18 \pm 3$  in 1970,  $10 \pm 2$  in 1980,  $5 \pm 1$  in 1990 and  $4 \pm 0.7$  by 1995.

### Emissions of Methyl Bromide from the Combustion of Leaded Gasoline

The contribution from bromine in leaded gasoline to atmospheric methyl bromide is highly uncertain. In studies using U.S. automobiles and "motor fluid," PbBrCl in

particulate form is the predominant form of lead emitted from automobile tailpipes, although lead oxides are also present [Hirschler *et al.*, 1957; Habibi, 1973, Ter Haar and Bayard, 1971]. However, quantitative determinations of the fraction of bromine emitted as PbBrCl, or in other forms, were not made.

Baumann and Heumann [1987] measured bromine emissions from a 1974 Opel Kadett C with no catalytic converter, using regular leaded gasoline, and with the car operating in neutral gear. They measured 90-190  $\mu\text{g}/\text{m}^3$  methyl bromide in the exhaust gas. Based on measurement of all of the emitted bromine, they concluded that 15-28% of the emitted bromine was methyl bromide. However, a mass balance calculation indicates that not all of the bromine in the gasoline was measured in the emissions, so the percentages may overestimate the emission factor.

Harsch and Rasmussen [1977] reported that exhaust from an automobile (1972 Rambler) using leaded gasoline contained 71-217  $\mu\text{g}/\text{m}^3$  of methyl bromide, consistent with the Baumann and Heumann result. Chakrabarti and Bell [1993] reported methyl bromide emissions of 370  $\mu\text{g}/\text{m}^3$ .

Hao [1986] measured methyl bromide emissions from a 1972 Ford LTD and a 1973 Dodge Dart at various driving speeds. He reported methyl bromide emissions of 120  $\mu\text{g}/\text{m}^3$  at idle, 20  $\mu\text{g}/\text{m}^3$  or less at speeds over 20 miles per hour, and emissions ranging from 4 to 520  $\mu\text{g}/\text{m}^3$  at 10 miles per hour. Neither the lead nor the bromine content of the gasoline were reported. The methyl bromide emission factor was reported as  $0.12 \pm 0.11\%$ , although it is not clear if this emission factor refers to the total driving cycle, or only to emissions at a fixed speed.

Total global emissions of methyl bromide are estimated to be about 180 kT/yr as of the early 1990s. The bromine used in gasoline —  $170 \pm 20$  kT/yr in the early 1970s, to  $23 \pm 2.5$  kT/yr in 1995 — could be a significant contributor to atmospheric methyl bromide. The Baumann and Heumann emission factor (BHEF) of 15-28% implies a global emission of  $43 \pm 14$  kT/yr of methyl bromide from leaded gasoline in 1970,  $26 \pm 8$  in 1980,  $17 \pm 5$  in 1985,  $10.2 \pm 3$  in 1990,  $7.6 \pm 2$  kT/yr in 1992-93, and  $5.7 \pm 1.7$  in 1995.

The temporal decrease of methyl bromide emissions from leaded gasoline combustion can be compared with the temporal

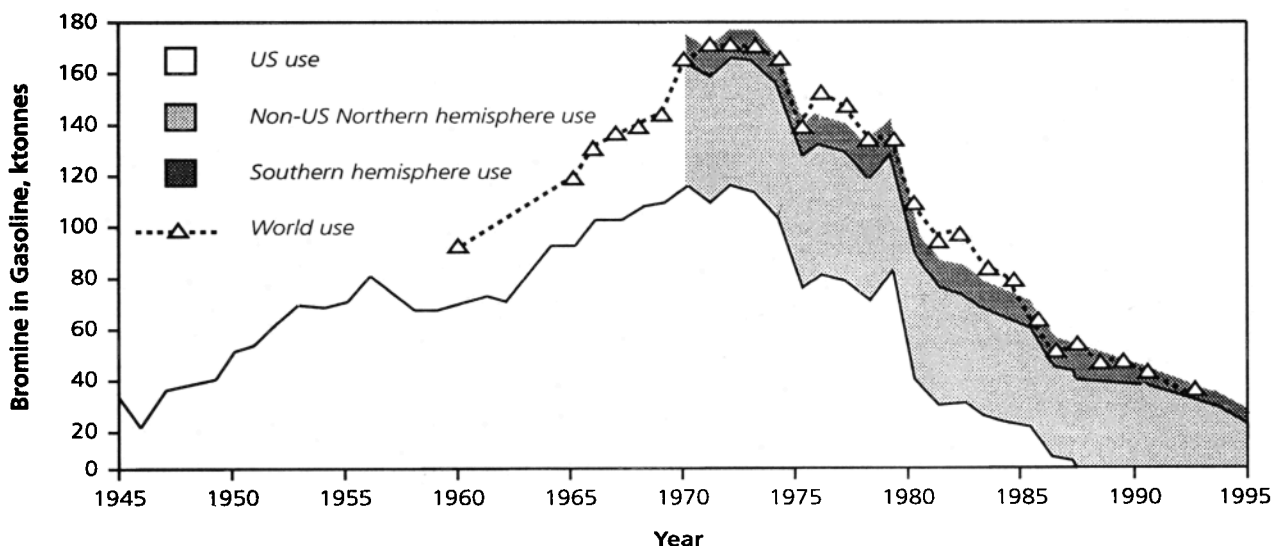


Figure 2. Estimated use of bromine in leaded gasoline. Quantities are based on data in Figure 1 and the estimated average Br:Pb weight ratio of  $0.45 \pm 0.05$ .

increase of synthetic methyl bromide used in agriculture. Global usage of  $\text{CH}_3\text{Br}$  for preplanting, post-harvesting and structural fumigation were 30, 9 and 2 kT in 1984, respectively. Corresponding figures for 1992 were 57, 10 and 2 kT [Penkett *et al.*, 1995]. Measured methyl bromide atmospheric emission factors from soil fumigation range from 34% to 80% [Yagi *et al.*, 1995], while the emission factor for post-harvest and structural fumigation is estimated to be 50% [Penkett *et al.*, 1995]. Thus between 1984 and 1992, atmospheric emissions of methyl bromide from all agricultural fumigation increased from 16-30 kT/yr to 25-52 kT/yr, for a net increase of 9-22 kT/yr. If the BHEF is correct, then methyl bromide emissions from leaded gasoline fell from about  $17 \pm 5$  to  $7.6 \pm 2$  kT/yr in the same period, for a decrease of about 9 kT/yr. In this case, at least 40% of the increase in agricultural emissions of methyl bromide could have been counterbalanced by decreased use of lead in gasoline. Similarly, if emissions from agricultural usage were 10 kT/yr in the early 1970s [Wofsy *et al.*, 1975] and they increased to 25-52 kT/yr in 1992, the drop in emissions from leaded gasoline usage (roughly 35 kT/yr with the BHEF) between 1970 and 1992 could have counterbalanced them.

However, if Hao's estimated emission factor of 0.1% is correct then global emissions from leaded gasoline would have ranged from 0.2 kT/yr in the early 1970s to 0.03 kT/yr in 1995. In this case, the combustion of leaded gasoline would be an insignificant contributor to global methyl bromide emissions. Carefully designed field and laboratory studies are needed to resolve uncertainty in the emission factor.

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