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Transfer of organic Br and Cl from the Biosphere to the Atmosphere during the Cretaceous/Tertiary Impact: Implications for the stratospheric Ozone Layer

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Abstract

Following the Cretaceous/Tertiary (K/T) meteoritic impact some 65 Myr ago, large portions of aboveground terrestrial biomass were burned. As a result, large amounts of various trace gases were injected to the atmosphere, inducing a wide range of effects on climate and ecosystems. Here, it is commented on the previously unaccounted emission to the atmosphere of methyl bromide (CH_3Br) and methyl chloride (CH_3Cl) from extensive biomass burning that followed the impact. Based on reported biomass burning emission rates of the above organohalogens relative to CO_2, it is estimated that their emissions from global fires resulted in tropospheric mixing ratios of around 20–65.8 ppbv organic Cl and 110–390 pptv organic Br. The above calculated mixing ratios of active chlorine and bromine are more than an order of magnitude their present, anthropogenically perturbed level and, although the ocean ultimately might absorb them, we argue here that they could still remain in the stratosphere for many years, substantially affecting the ozone layer. This would have lead to very serious increases in short wavelength UV radiation reaching the lowermost atmosphere.

1. Introduction

Atmospheric consequences of meteoritic impacts have been discussed by a number of researchers (see review by Toon et al., 1997). These consequences include climatic and chemical effects in the troposphere and the stratosphere. Massive impacts, with energies $>10^7$ Mt, occur at intervals of approximately 10^7 yrs and the ejecta re-entering the atmosphere can lead to massive global fires that can burn a major part of the terrestrial aboveground biomass. Reported stratospheric impacts of bolides $>10^7$ Mt result from injections of dust, NO and water vapour in the stratosphere. Ozone loss is then a consequence of enhanced NO levels and accelerated heterogeneous chemistry. After the removal of radiation-blocking dust, smoke and NO_2 from the atmosphere, significantly increased doses of UV-B radiation could reach the ground for periods up to

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several years as a result of ozone depletion. However, if a shielding layer of stratospheric sulphate particles forms, much of the UV-B may be blocked from reaching the surface the first few years after the impact.

Tropospheric effects might be even more serious. During the K/T boundary event some 65 Myr ago which is currently believed to have been caused by an object with impact energy of the order of 10^8–10^9 Mt, 3×10^{17}–3×10^{18} gr NO might have been produced. These NO levels could cause mass extinctions through a series of effects, the most serious of these being extensive acidification of surface soils and waters due to the precipitation of nitric acid (HNO_3), produced by the atmospheric degradation of NO (Prinn and Fegley, 1987; Crutzen, 1987).

It is believed that a major fraction of the aboveground biomass burned after the K/T impact from fires ignited by ejecta re-entering the atmosphere (Kring and Durda, 2002). This is because of a worldwide soot layer at the K/T boundary (Wolbach et al., 1990a, b), carbon isotope shifts (Ivany and Salawitch, 1993) and a widespread, sharp peak in the distribution of fern spores (Wolfe and Upchurch, 1986), the latter usually taken as a sign of wildfires. Extrapolating from the discovery of 5×10^6 g of soot in K/T clays (Wolbach et al., 1990a, b), Crutzen (1987) estimated that global fires following the impact have produced more than 10^{19} g CO_2, 10^{18} g CO and a variety of other gases, including pyrotoxins.

Methyl bromide and methyl chloride have not yet been included in the calculated trace gas emissions to the atmosphere during the K/T impact. However, these gases are sufficiently long-lived to enter the stratosphere, where they release active chlorine and bromine, which catalytically destroy ozone. Here, recent reports of CH_3Br and CH_3Cl emissions from biomass burning are used to calculate the amounts of these gases that would have been released from the global fires of the K/T impact event.

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2. Results and discussion

The halogenated gases CH_3Cl and CH_3Br deliver Cl and Br, respectively, to the stratosphere, where they can catalytically destroy ozone (e.g. Fabian et al., 1994; Kourtidis et al., 1998; Montzka and Fraser, 2003). CH_3Cl is the most abundant halocarbon in the atmosphere, with a NH (SH) average mixing ratio around 536 (541) pptv (Simmonds et al., 2004), corresponding to an atmospheric global burden of about 4.3 Tg. Biomass burning might presently be the single largest source of methyl chloride ($1.0\pm0.3\times10^{12}$ g yr^{-1}, Andreae et al., 1996; Blake et al., 1996; Lobert et al., 1999), followed by oceanic emissions ($0.3\pm0.1\times10^{12}$ g yr^{-1}, Moore et al., 1996; 0.65×10^{12} g yr^{-1}, Khalil et al., 1999) and fungal production (0.16×10^{12} g yr^{-1}, Watling and Harper, 1998). The amounts of methyl halides produced during biomass burning are related to the Cl/Br content of the biomass, which again depends on the soil Cl/Br content (Andreae et al., 1996; Gan et al., 1998). Sinks of methyl chloride are OH attack in the troposphere (-3 Tg yr^{-1}) and, to a lesser extend, oceanic uptake (-0.2 Tg yr^{-1}). CH_3Br exists currently in the atmosphere at a NH (SH) mixing ratio of 10.4 (7.9) ppt (Simmonds et al., 2004), corresponding to an atmospheric global burden of about 146 Gg. Manö and Andreae (1994) first reported biomass burning as a source of methyl bromide. This source delivers currently 10–24 Gg yr^{-1} (best estimate 20 Gg yr^{-1}) CH_3Br to the atmosphere and is thus responsible for around 20% of total global emissions of CH_3Br (Andreae et al., 1996; Blake et al., 1996). Sinks of methyl bromide other than the oceans include reaction with OH and photolysis (-86 Gg yr^{-1}) and uptake by soils (-42 Gg yr^{-1}, Shorter et al., 1995).

Andreae et al. (1996) during the SAFARI-92 experiment and Blake et al. (1996) during the TRACE-A experiment have measured relative emission ratios of methyl halides. Andreae et al. (1996) report emission ratios of CH_3Cl relative to CO_2 and CO of 20 ppt/ppm and 0.95 ppt/ppb, respectively, and emission ratios of CH_3Br relative to CO_2, CO and CH_3Cl of 0.11 ppt/ppm, 8.3×10^{-3} ppt/ppb and 8.3 ppt/ppb, respectively Blake et al. (1996) measured emission ratios of CH_3Cl relative to CO_2 and CO

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of 27–37 ppt/ppm and 0.57–0.85 ppt/ppb, respectively, and emission ratios of CH_3Br relative to CO_2 and CO of 0.37–0.39 ppt/ppm and $6-10.6\times10^{-3}$ ppt/ppb. Lobert et al. (1999), after a compilation of all available data, arrived at a significantly higher median emission ratio of CH_3Cl relative to CO_2 of 65.8 ppt/ppm. Hence pyrogenic CH_3Br and CH_3Cl emissions are today considered as significant contributors to stratospheric ozone depletion, constituting roughly 25% and 20% of present-day global CH_3Cl and CH_3Br emissions, respectively (Andreae et al., 1996; Blake et al., 1996). Other authors also reported relative emission ratios of CH_3Cl to CO and CO_2 (see compilation by Lobert et al., 1999, and references therein). As noted above, shortly after the K/T impact, around 10^{19} gr of CO_2 have been emitted to the atmosphere from extensive global fires, about 3 times the amount of CO_2 currently in the atmosphere, i.e. globally around 1000 ppm CO_2 have been injected to the troposphere (Crutzen, 1987).

Hence, by using the abovementioned emission rates relative to CO_2, we calculate that the amounts of CH_3Cl and CH_3Br that have been released into the atmosphere would have resulted in global tropospheric volume mixing ratios (VMRs) of around 20–65.8 ppbv of CH_3Cl and 110–390 pptv CH_3Br after the K/T impact. The above-calculated VMRs of methyl chloride are 36–120 times the present level of about 550 pptv, while the methyl bromide VMR is 11–39 times the present level of about 10 pptv. Considering that these levels translate to 20–65.8 ppbv of active chlorine and 110–390 pptv of active bromine, and that the present-day, anthropogenically perturbed levels of organic chlorine and bromine are around 3.6 ppbv and 20 pptv, respectively (Montzka and Fraser, 2003), these levels would have seriously damaged the stratospheric ozone layer, since they are 5.6–18.3 times and 5.5–19.5 times, respectively, of these levels..

Whether such damage to the ozone layer occurred or not, ultimately would depend on:

1. The efficiency of tropospheric removal through reactions with OH, if large amounts of CH_3Cl and CH_3Br do not reach the stratosphere soon after the impact. The tropospheric lifetime of these two gases is presently determined by the hydroxyl

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radical (OH) abundance. Due to the burning of substantial portions of above-ground biomass, concurrently with the release of CH_3Cl and CH_3Br, substantial amounts of smoke and radiation-absorbing gases (like NO_2) will be emitted to the atmosphere. Smoke and absorbing gases will block solar radiation, and OH production from the photodissociation of tropospheric ozone will either stop or be reduced substantially. This, combined with fast consumption of OH from emitted hydrocarbons, will lead to OH levels near zero and hence very long tropospheric lifetimes for CH_3Cl and CH_3Br until the smoke veil disappears.

2. The efficiencies of tropospheric removal through reactions on particles, if large amounts of CH_3Cl and CH_3Br do not reach the stratosphere soon after the impact. Heterogeneous tropospheric and stratospheric chemistry after such an explosion would be greatly perturbed (see review by Toon et al., 1997). It cannot be said with certainty whether the removal of the above gases from the atmosphere through heterogeneous reactions on tropospheric particles would substantially deplete them since, to our knowledge, no kinetic data exist that would allow for a quantification of this effect. However, since most published data on relative emission rates of these methyl halides from biomass burning are from in-situ observations of plumes, young or aged, uptake on particles, if any, is likely already included in our calculations.

3. The efficiencies of tropospheric removal through oceanic uptake, if large amounts of CH_3Cl and CH_3Br do not reach the stratosphere soon after the impact. How fast and whether oceanic uptake would reduce significantly the atmospheric burden would depend on a number of factors, related to the biological, chemical and thermal state of the ocean after the impact, some of which are poorly constrained. Namely, we do not know a) whether the massive die-off of phytoplankton that occurred after the impact (e.g. Kaiho et al., 1999) would have released copious amounts of intracellular methyl bromide and methyl chloride in the sea water. This would temporarily reduce the degree of ocean undersaturation, or might even

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have resulted in supersaturation with respect to the atmosphere. b) We do not know the degree of inhibition of vertical mixing after the impact. If vertical mixing was seriously reduced, stratification of the upper ocean layer would inhibit the loss of surface water organohalogens to the ocean below, resulting in quick saturation of the upper layer.

Here, we use a two-box ocean-atmosphere model and some reasonable assumptions to calculate the effect of ocean uptake.

The model is identical to that in Butler (1994). Ignoring transport, the general equations governing the coupled ocean-atmosphere system are (Butler, 1994; Yvon and Butler, 1996):

$$\frac{dn_a}{dt} = S_A + F_l + F_{oa} - F_a - F_s \tag{1}$$

or

$$\frac{dn_a}{dt} = S_A + F_l + F_{oa} - F_{OH} - F_s\,, \tag{1'}$$

$$\frac{dn_o}{dt} = P_o - F_{oa} - F_d - F_{ed}\,, \tag{2}$$

where n_a and n_o are the mole mass of CH_3Br in the atmosphere (equal to p_aM, where p_a is the atmospheric partial pressure of CH_3Br at sea level in patm and $M=1.79\cdot10^{20}$ mol is the mass of the atmosphere) and in the surface ocean (equal to p_wAz/H), respectively, S_A is the anthropogenic source flux (moles·y^{-1}, set equal to zero), F_l is the flux from non-anthropogenic, land-based sources (e.g. biomass burning) (moles·y^{-1}, also set to zero), F_{oa} is the net flux from the ocean to the atmosphere (moles·y^{-1}), F_a is the atmospheric loss rate of CH_3Br (moles·y^{-1}), which equals to the loss rate due to reaction with OH, F_{OH}, F_s is the loss to soils or plant canopies (moles·y^{-1}, also set to zero), P_0 is the production of CH_3Br in the ocean (moles·y^{-1})

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($P_0 = p_0 \cdot A$, where p_0 is the production rate in the ocean in moles·m^{-2}·y^{-1} and A is the entire surface area of the ocean and equal to $3.61 \cdot 10^{14}$ m^2), F_d is the aquatic degradation rate (moles·y^{-1}), and F_{ed} is the loss rate of CH_3Br from combined downward mixing and degradation through the thermocline (moles·y^{-1}).

The analytical expressions of Eqs. (1) and (2) are

$$\frac{dn_a}{dt} = S_A + F_l + \frac{K_w A}{H}(p_w - p_a) - k_a n_a - k_s n_a \tag{3}$$

or

$$\frac{dn_a}{dt} = S_A + F_l + \frac{K_w A}{H}(p_w - p_a) - k_{OH} n_a - k_s n_a \tag{3'}$$

$$\frac{dn_o}{dt} = P_o - \frac{K_w A}{H}(p_w - p_a) - k_d n_o - \frac{k_{ed}}{z} n_o \tag{4}$$

or

$$\frac{dn_o}{dt} = P_o - \frac{K_w A}{H}(p_w - p_a) - k_d n_o - \frac{\sqrt{D_z k_d}}{z} n_o\,, \tag{4'}$$

where k_d is the pseudofirstorder loss constant for aquatic degradation in the surface layer (36 y^{-1}), K_w is the mean air-sea exchange coefficient ($1.5 \cdot 10^3$m·y^{-1}), p_a is the partial pressure of CH_3Br (atm) in the atmosphere at sea level and p_w is the mean oceanic partial pressure of CH_3Br in patm, H is Henry's Law constant (m^3·atm·mole^{-1}), k_{ed} is the "eddy degradation" rate for removal of CH_3Br downward from the surface layer (440 m·y^{-1}), z is the thickness of the surface layer (m), k_a is the pseudo-first-order loss constant for the degradation in the atmosphere, and if we treat only the reaction with OH it equals k_{OH} (the CH_3Br stratospheric loss has a rate which is slow compared to OH and is ignored here).

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The depth of the surface mixing layer is assumed to be constant and equal to 75 m, while the eddy diffusion rate of removal, k_{ed}, is given by

$$k_{ed} = (D_z k_d)^{0.5}, \tag{5}$$

where the mean diffusivity through the thermocline, D_z, is equal to 5440 m·y^{-1}.

The most significant tropospheric removal pathway for CH_3Br is the reaction with the hydroxyl (OH) radical, which determines the lifetime of CH_3Br in the atmosphere. A mean OH tropospheric concentration of 10^6 molecules cm^{-3} and a reaction rate of $k_{OH}=1.86\cdot10^{-12}\cdot e^{-1230/T}$ cm^3·molecule^{-1}·s^{-1} were used (Chichinin et al., 1994).

The main aquatic chemical degradation pathways for CH_3Br are hydrolysis and nucleophilic substitution by Cl^-, the latter being the main destruction pathway,

$$CH_3Br + Cl^- \rightarrow CH_3Cl + Br^-$$

$$CH_3Br + H_2O \rightarrow CH_3OH + H^+ + Br^-$$

at a typical oceanic surface temperature of 21.9°C, [Cl]=0.56 moles·liter^{-1}. For k_{H_2O} and k_{Cl}, the values by Jeffers and Wolf (1996) were used, $k_{H_2O}=5.7\cdot10^{11}\cdot e^{-(12\,455\pm240)/T}$ s^{-1}, $k_{Cl}=1.09\cdot10^{13}\cdot e^{-(12\,724\pm560)/T}$ l mol^{-1}·s^{-1}.

Equations (3′) and (4′) were solved numerically by Euler's method. As the model is formulated, CH_3Br is produced solely in the ocean. In the basecase run, we used a P_0 value of $6.0\cdot10^{-6}$ mol m^{-2}y^{-1}, half of the sum of P_0 in the open ocean, $3.9\cdot10^{-6}$ mol m^{-2} y^{-1}, and the coastal water, $8.0\cdot10^{-6}$ mol m^{-2}y^{-1}, as given by Butler and Rodriguez (1996). We also consider that the removal of atmospheric CH_3Br takes place only by its reaction with OH and by ocean-atmosphere exchange. Depending on the initial conditions, the latter process is a sink or a source of atmospheric CH_3Br. The soil sink as well as newly discovered sources from coastal salt marshes, plants, wetlands and natural oxidation processes during degradation of Fe-containing organic matter were not considered, since they were unimportant in the perturbed conditions

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after the K/T impact. Hence in the present study $S_A=F_l=F_s=0$. Possible oceanic and atmospheric heterogeneities, such as the different mixing depth z and the spatiotemporal variability of Cl^- and OH concentrations, were ignored. The surface ocean was treated uniformly and had a surface area of $3.61 \cdot 10^{14}$ m^2.

To investigate the possible development of tropospheric CH_3Br in time after the initial emission from the massive impact fires, different scenarios were modelled (Table 1 and Fig. 1). These scenarios can give insight into the possible development of CH_3Br concentrations during post-impact conditions. Although only the lower limit of initial releases was modelled (110 pptv), for other concentrations the relative development will be rather similar. Due to the absence of a relevant model for CH_3Cl, only CH_3Br was modelled.

Under present-day conditions (Scenario 1), CH_3Br is removed from the atmosphere rather fast due to OH oxidation. Under perturbed conditions (Scenarios 2 to 8), although we assumed that oceanic production ceases or is greatly diminished, CH_3Br is removed more slowly due to the assumed reductions in the oxidation capacity of the atmosphere. Scenarios 3, 4, 5 and 6 show quite similar developments during the first 4 years. For these scenarios, where oceanic production of CH_3Br ceases or is halved and atmospheric oxidation is halved concurrently with changes in mixed layer depth, around 1/3 of CH_3Br still remains in the atmosphere after 2 years.

If atmospheric oxidation ceases completely for the simulation period (Scenario 2), around 1/3 of CH_3Br still remains in the atmosphere after 6 years. This is an improbable scenario, but demonstrates the strong influence of the oxidising capacity of the atmosphere on the post-impact development of tropospheric CH_3Br. If we assume at the same time that large amounts of intracellular CH_3Br is released in the seawater due to the massive death of plankton (Scenario 8), then tropospheric CH_3Br decreases even more slowly, due to the decrease of its flux across the air-sea interface.

Finally, scenario 7 models a more probable development. We assume that oceanic production ceases for 10 years, and then slowly recovers at 30% its present-day value. The oxidising capacity of the atmosphere (as determined from OH concentrations)

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ceases for the first year due to the large amounts of smoke that block incoming radiation, and then slowly recovers as the smoke settles (see Table 1). We also assume that the ocean is more stratified and the mixed layer depth is halved, although this latter assumption will not have a major effect in the development of tropospheric CH_3Br, as simulations 5 and 6 have shown. For this scenario, more than half of the initially released CH_3Br still remains in the atmosphere after 2 years; after 4 years, about 1/4 is still in the atmosphere.

Hence, although ultimately the initially released tropospheric CH_3Br will be removed due to oxidation and absorption by the ocean, this removal will take some years to occur. It is important, however, to stress that ultimately, damage on the ozone layer would depend largely on the efficiency of a fourth process, namely direct transport of the emitted amounts to the stratosphere. Transport to the stratosphere would certainly be influenced by the perturbed thermal state of the atmosphere. It has been argued, that fire-convection can entrain trace gases and smoke to the stratosphere (Fromm et al., 2004). Kao et al., 1990, modelled post-nuclear war conditions taking into account solar heating of the smoke plume. In their treatment, because very little sunlight reaches the surface the first days after the nuclear blasts a thermal inversion occurs which prevents downward diffusion of heat and, additionally, sunlight heats the top of the smoke cloud making the atmosphere above unstable, thus lofting the plume (Kao et al., 1990). Indeed, smoke from California fires in 1987 has been observed to strengthen a valley inversion cooling the surface by several degrees (Robock, 1988). Recently, smoke from fire plumes has been detected in the lower stratosphere (Fromm et al., 2000) and carbon monoxide and particles unambiguously attributed to North American fires were detected several kilometres above the extratropical tropopause (Jost et al., 2004). Proposed mechanisms responsible for the transport include convective systems inertial overshooting of the neutral buoyancy level, additional radiative self-heating of the plumes and subsequent lofting (Jost et al., 2004), as well as solar-driven lofting of smoke-filled air (Kao et al., 1990). Kring and Durda (2002) have calculated that the power delivered to the atmosphere by re-entering high-energy ejecta would have

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been in some areas in excess of 100 kWm^{-2}, with a peak of around 350 kWm^{-2} (see Kring and Durda, 2002, for details of the simulations), while the power delivered to the ground would be in excess of 12.5 kWm^{-2} for >20 min (the amount of energy sufficient to ignite vegetation). The dissipation of such large amounts of energy, both from the re-entering ejecta and the subsequent global fires would probably involve also intensification of vertical mixing and might also be sufficient to cause tropospheric folding in some areas and maybe even complete break-up of the tropopause barrier. Such Stratosphere-Troposphere Exchange (STE) events would bring large amounts of the emitted gases from the troposphere to the stratosphere, although it is not possible to quantify the exact extent of such STE events.

It thus appears very plausible that a large amount of the emitted methyl halides could reach the stratosphere, causing serious damage to the ozone layer for the following decades. The resulting ozone depletion should have influenced the transfer of solar UV through the atmosphere. Increases in UV would not reach the ground before tropospheric soot particles settle, as much of the radiation would be scattered by the particles with an optical depth of around 10^3–10^4 (see review by Toon et al., 1997). Spherical particles with a density of 3 gcm^{-3} falling in a Stokes regime from 85 km altitude would require more than a decade to settle if they have a radius of 1 μm and an hour if they have a radius of 1 mm (H. J. Melosh, cited in Fig. 12 of Kring and Durda, 2002). These are upper time limits, since coagulation of particles into larger grains was not considered. Other calculations suggest that a significant portion of sub-micron dust would have remained in the atmosphere for several months, causing reductions in the light levels reaching the ground (e.g. Covey et al., 1990). It is unlikely that impact dust would cause much reduction in the UV part of the spectrum, except perhaps for the initial phase, when it would be denser. This is because dust causes attenuation mainly in the visible and UV-A part of the spectrum, while the shorter UV-B wavelengths remain unaffected (e.g. Madronich, 1993), as has been shown, for example, during Saharan dust events (Balis et al., 2002).

Ozone loss during such impacts is not presently considered the major threat to the

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biosphere, mainly because it has been assumed that ozone depletion would result from NO injections to the stratosphere. These would perturb the ozone layer, but any increase in UV radiation reaching the ground would be prevented by the shielding from smoke, dust, absorbing gases and a stratospheric sulphate particle layer that would form from the injection of large amounts of SO_2. Smoke and dust would settle after a few months, and the sulphate layer would also settle after a few years. Following the large eruption of volcanoes such as Pinatubo, the sulphate layer that formed had a persistence of about 2 years. After that period, significant doses of UV might reach the ground, but this effect would not last long since NO would also be removed from the stratosphere through conversion to HNO_3 and absorption on particles.

However, the calculations and argumentation presented in this manuscript imply that the ozone layer could be depleted considerably by the release of such large amounts of relatively long-lived CH_3Br and CH_3Cl in a stratosphere already perturbed by large amounts of NO and particles. Such injections could raise the atmospheric abundance of natural organic chlorine and bromine an order of magnitude above their levels in the present-day, CFC and Halon-containing atmosphere. Ozone depletion will take place during the first years after such an impact in a stratosphere heavily loaded with aerosols and NO. CH_3Cl and CH_3Br have presently an overall atmospheric lifetime of around 1.5–2 years. Because the inverse overall lifetime is the sum of the inverse stratospheric and tropospheric lifetimes, their overall lifetimes are primarily determined by their short (1.5–2 years) tropospheric lifetime, while their stratospheric lifetimes are considerably longer. CH_3Cl has a stratospheric lifetime of around 50 years, while CH_3Br has a somewhat lower stratospheric lifetime. The stratospheric lifetimes of the two species are quite long, compared with the lifetime of stratospheric aerosols of around one year and a lifetime for tropospheric aerosols on the order of a few days. The consequences of these organohalogen releases would be more persistent than aerosol injections and hence radiation enhancements due to the ozone depletion from natural organohalogens could outlive the sulphuric aerosol layer, if the ocean will not take up large amounts off their atmospheric burden. When the UV-B shielding of the

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aerosol layer ceases, considerable enhancements in short-wavelength UV radiation reaching the ground could then persist for decades.

3. Conclusions

The results from the presented calculations indicate that following the K/T impact, methyl bromide and methyl chloride emissions from biomass burning were of a magnitude that could seriously damage the ozone layer and as a consequence the penetration of short-wavelength solar radiation. A better study of the processes controlling the oceanic fluxes of these compounds and a better knowledge of the thermal and chemical state of the atmosphere and the ocean following the impact could offer more constrain of the calculations presented here.

While impacts such as the K/T one occur at intervals of 10^7 yrs, more frequent, less massive events could ignite a smaller portion of global forests. If one-tenth of the forests ignited during the K/T event are burned, CH_3Cl and CH_3Br levels might rise by 3.6–12 times and 1.1–3.9 times their present level, respectively. Global nuclear war could also cause extensive forest burning, although one should then bear in mind that present-day above-ground biomass density is around 1/3 of the K/T one. It appears that pyrogenic emissions of these organohalogens might also in such cases influence the ozone layer and should be included in relevant simulations.

Only very recently some attention was given to the possible role of organohalogens in earth history (Yokouchi et al., 2002). The present study shows that there more reason for the study of these gases in such a perspective.

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Table 1. The different model scenarios. P_o is the CH_3Br biological production in the surface ocean, T_a is the atmospheric temperature, and z is the mixed layer depth. The temperature of the oceanic surface layer, T_o, was set to 288°K. The initial tropospheric molar ratio of CH_3Br was set at 110 pptv.

Scen. Nr.	P_o ($6 \cdot 10^{-6}$ mol $m^{-2}y^{-1}$)	T_a (°K)	Sea conc. (pmol·mol^{-1})	[OH](10^6 molecules ·$cm^{-3} \cdot 10^6$)	Z (75 m)	Case
1	1	290	5	1	1	Base case (present-day conditions)
2	0	290	5	0	1	Oceanic production and atmospheric oxidation cease
3	0	290	5	0.5	1	Oceanic production ceases and atmospheric oxidation is halved
4	0.5	290	5	0.5	1	Oceanic production and atmospheric oxidation are halved
5	0	290	5	0.5	0.5	Oceanic production ceases, atmospheric oxidation is halved and the mixing layer depth is halved
6	0	290	5	0.5	–	Oceanic production ceases, atmospheric oxidation is halved and there is no loss through the thermocline
7	0 for 10 yr, 0.3 afterwards	290	5	0 until yr 1, 0.2 until yr 3, 0.6 until yr 6, 1 afterwards	0.5 until yr 1, 0.7 until yr 3, 1 afterwards	Mixed scenario
8	0	290	50	0	0.5	Oceanic production and atmospheric oxidation cease, the mixing layer depth is halved and the sea conc. is raised due to release of intracellular CH_3Br

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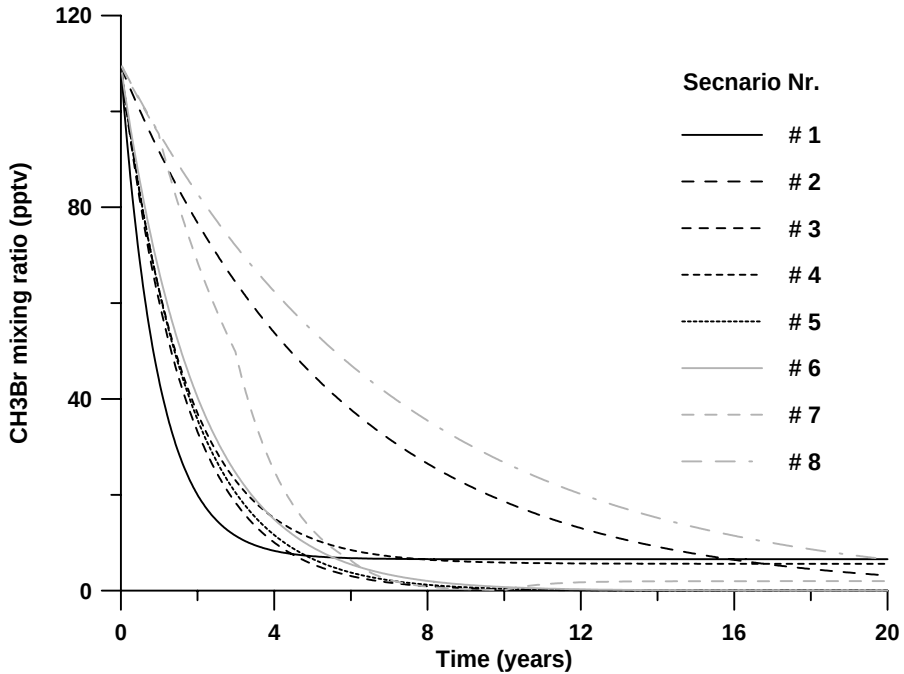

Fig. 1. Box-model calculations, for different scenarios (see Table 1), of the evolution of the tropospheric burden of CH_3Br after its initial release from biomass burning. The initial tropospheric molar ratio of CH_3Br was set at 110 pptv, which is a lower limit for the initial release.

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