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Atmospheric lifetimes of trace gases

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The atmospheric concentration of a trace gas is determined by the balance between its sources and sinks. However, the sink processes alone determine the lifetime (residence time) of the gas in the atmosphere. This Environmental Brief outlines how lifetimes are calculated and presents some caveats about their interpretation.

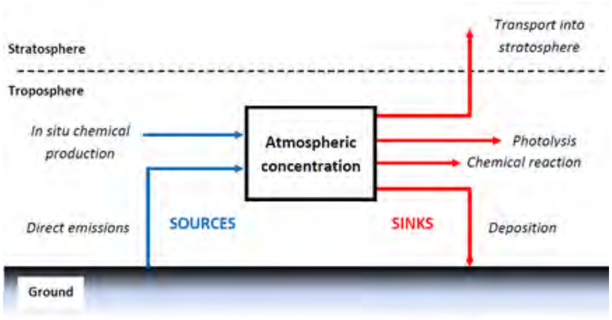

Figure 1: *A summary of atmospheric sources and sinks. Note that this particular model neglects physical transport of trace gases into and out of the central box.*

Many trace gases are emitted directly into the atmosphere (**Figure 1**). Examples for these primary emissions include nitrogen oxides (NO_x = NO + NO_2) from fossil fuel combustion and vehicle exhausts, and hydrocarbons of both biogenic and man-made origin. Primary emissions generally enter the atmosphere from sources located on the Earth's surface, and so this Brief concentrates on tropospheric chemistry. A second subset of trace gases is generated *in situ* by chemical and photochemical processes within the atmosphere: for example, tropospheric ozone is a secondary pollutant. Trace gases are removed by various sink processes. Reactive species (such as ozone) or soluble species (such as nitric acid) are deposited by contact with the ground; carbon dioxide is taken up by plants. A few chemically important molecules (notably ozone and NO_2) undergo photolysis in the troposphere (1). However, the main sink for most trace gases is reaction with a tropospheric oxidant such as OH or NO_3 radicals (1, 2). Only those compounds that do not photolyse and do not react with tropospheric oxidants (or do so only slowly) persist long enough to be transported into the stratosphere, chlorofluorocarbons being pertinent examples.

Lifetimes

To understand the concept of a lifetime, consider a trace gas that is removed from the atmosphere *via* a single sink process characterised by a first-order rate coefficient k (with units 1/time). Suppose also that the sink balances the sources of this trace gas, so its concentration is stable (**Figure 2**). Next, suppose that an instantaneous, extra pulse of the trace gas (P_0) enters the atmosphere: this occurs at Year 2 in **Figure 2**. The amount of extra gas is so small that it does not perturb other atmospheric processes. After the pulse, the excess concentration P decays exponentially with time as the concentration of the trace gas re-establishes steady-state:

$$P = P_0 \exp(-kt) \qquad \text{(eq. 1)}$$

Recasting eq. 1 in terms of a decay time constant t gives

$$P = P_0 \exp(-t/\tau) \qquad \text{(eq. 2)}$$

Thus the atmospheric lifetime of the gas is the inverse of the first-order rate coefficient for its sink process:

$$\tau = 1/k \qquad \text{(eq. 3)}$$

Figure 2 illustrates another important result. The amount of extra gas emitted is the same in the two cases shown, but whereas the short-lived gas essentially re-establishes its steady-state concentration within five years of the emission event, the effects of the long-lived gas persist for decades. It is no coincidence that the major greenhouse gases (CO_2, CH_4 and N_2O) implicated in anthropogenic climate change are long-lived.

The same concept can be applied to a trace gas with multiple sinks, except now the rate coefficient is the sum of the first order rate coefficients characterising each of the various sink processes, as given in eq. 4. By analogy with eq. 3, the overall atmospheric lifetime is given by the reciprocal of the sum of the reciprocal lifetimes for

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each sink process (eq. 5). Note that the overall lifetime is necessarily shorter than even the shortest lifetime characterising the fastest sink process.

$$K_{\text{total}} = k_1 + k_2 + k_3 + \ldots \qquad \text{(eq. 4)}$$

$$1/\tau_{\text{total}} = 1/\tau_1 + 1/\tau_2 + 1/\tau_3 + \ldots \qquad \text{(eq. 5)}$$

For example, methyl chloroform (CH_3CCl_3) has lifetimes of 6.0 years for loss by reaction with OH, 38 years for loss into the stratosphere and 94 years for deposition to the ocean (3). $1/\tau_{\text{total}} = 1/6.0 + 1/38 + 1/94 = 0.204$ year^{-1} and so the overall lifetime is $\tau_{\text{total}} = 1/0.204 = 4.9$ years.

Chemical loss

The rate-limiting step in the atmospheric degradation of very many trace gases is their reaction with OH radicals during the day. The lifetime of a trace gas A with respect to reaction with OH is

$$\tau_{OH} = 1/(k_{OH} \times [OH]) \qquad \text{(eq. 6)}$$

where k_{OH} is the rate coefficient for the second-order reaction A + OH → products and [OH] is the atmospheric concentration of OH radicals. An analogous expression provides the lifetime for oxidation by NO_3 radicals at night. Reaction with ozone and chlorine atoms can also sometimes initiate oxidation of trace gases.

For example, OH reacts with isoprene (emitted by plants) with a rate coefficient $k_{OH} = 1.0 \times 10^{-10}$ molecule^{-1} cm^3 s^{-1} at 298 K (4). Assuming an average [OH] of 2×10^6 molecules cm^{-3} during daylight (= 12 hours), eq. 6 yields $\tau_{OH} = 1.4$ hours. Note here τ_{OH} is the day-time lifetime of isoprene's loss *via* OH: at night, [OH] is zero and τ_{OH} is thus indefinite. Isoprene also reacts with NO_3 ($k_{NO3} = 7.0 \times 10^{-13}$ molecule^{-1} cm^3 s^{-1} at 298 K (4)). Eq. 6 gives $\tau_{NO3} = 0.8$ hours assuming $[NO_3] = 5.0 \times 10^8$ molecules cm^{-3} at night (= 12 hours). Since $[NO_3]$ is zero in daylight (2), τ_{NO3} is indefinite during the day. The mean lifetime of isoprene over the 24-hour diurnal cycle is ≈ 1.1 hours.

Caveats

The simple analysis outlined above has some problems. In particular, eq. 6 predicts the lifetime of methane to be 5.0 years using $k_{OH} = 6.4 \times 10^{-15}$ molecules^{-1} cm^3 s^{-1} at 298 K (4) and a representative 24-hour average of [OH] $= 1 \times 10^6$ molecules cm^{-3}. (Methane does not react with NO_3). However, methane's lifetime for OH oxidation is widely accepted to be a factor of two longer: e.g. 9.7 years (5). The discrepancy arises in part from having used the 298 K rate coefficient in eq. 6. Reactions of OH or NO_3 with hydrocarbons have an activation energy barrier, and hence the rate coefficients decrease with decreasing temperature (4). Outside of equatorial regions and summertime temperate regions, temperatures are below 298 K and methane's lifetime is correspondingly longer. Vertical mixing of methane to higher and hence cooler altitudes also considerably prolongs its lifetime (5).

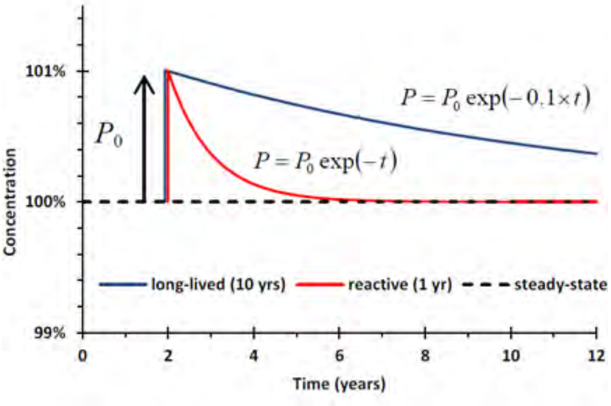

Figure 2: *Concentration-time profiles for gases with lifetimes of 1 and 10 years.*

Another major issue concerns what OH concentration to use in eq. 6. OH concentrations peak around midday and tail off to zero at sunrise and sunset; the assumption of a constant mean OH concentration is a gross simplification. OH concentrations also vary with the seasons due to the differences in solar zenith angles and the number of hours of daylight. In practice, methane's atmospheric lifetime is negligibly influenced by diurnal and seasonal variations in OH because methane is sufficiently long-lived for these effects to average out (5), but such OH variations are important for shorter-lived species. Methane's lifetime instead depends on latitudinal variations in OH, and equatorial regions have the highest OH concentrations. These factors, allied to the temperature dependence of the OH + CH_4 reaction rate, result in 60% of global methane being oxidised between 30°S and 30°N at altitudes between the ground and 5 km (5). The global atmospheric lifetime of methane is best estimated from a weighted average of methane lifetimes calculated over different latitudes and altitudes.

References

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