SHOULD GLOBAL TROPOSPHERIC VAPOR CONCENTRATIONS BE RECORDED ON A MASS DENSITY BASIS?

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Abstract. Extensive databases of tropospheric trace vapor concentrations have been published in the technical literature. In contrast to data reported in units of partial pressure, volume fraction, mole fraction, or mass concentration normalized to a reference temperature, data reported on an unnormalized mass concentration basis may exhibit a variation of as much as 50% when data from equatorial areas are compared with data from polar regions. Secondly, changes in tropospheric temperature are likely to yield variations in unnormalized mass concentration data substantially greater than variations attributable to either changes in surface air pressure or relative humidity. Lastly, atmospheric aerosol data also may be subject to these phenomena.

INTRODUCTION

The global atmospheric transport of natural and anthropogenic gases has been of concern to environmental professionals investigating such diverse areas as stratospheric ozone depletion, global warming and contamination of pristine ecosystems by persistent, bioaccumulative and toxic compounds. In an effort to better understand these issues, investigators have engaged in extensive research efforts focusing on the development of both regional/global atmospheric transport models (e.g., Scheringer et al., 2000) and rigorous experimental databases of atmospheric vapor concentrations. These databases are used to assess the risks resulting from atmospheric trace vapor transport and to test the validity of the transport models. The transport models typically link atmospheric circulation algorithms with process models designed to estimate trace vapor gener-ation/deposition/degradation, air/water exchange, and air/soil exchange.

The experimental databases used to assess both risks and global transport models typically contain records of trace vapor concentrations in addition to a host of common environmental variables. Published trace vapor concentration data have been reported in a number of units including: raw mass per unit volume, mass per unit volume normalized to STP, atmospheric partial pressure, volume fraction and mole fraction. We will present evidence suggesting that although sometimes found in the technical literature, the practice of recording atmospheric trace vapor concentrations in unnormalized units of mass/volume may impart an unintended (and unnecessary) variation to published global latitudinal trace vapor concentration gradients.

The ideal gas equation is fundamental to the thermodynamic understanding of the properties of gases:

$$PV = nRT \qquad (1)$$

where P = pressure, R = ideal gas constant, V = volume, T = absolute temperature and n = number of moles of gas present. This equation is frequently used to assess the conditions under which a gas exhibits ideal behavior. Equation (1) also can be rearranged to yield:

$$P = (n/V)RT = DRT \qquad (2)$$

where D represents the mole density of the gas. If D is multiplied by the molecular weight of the gas, then the mole density in equation (2) is converted to a mass density. Sutton (1961) suggests that equation (2) (with appropriate factors) is a reasonable model for estimating atmospheric gas densities for most meteorological purposes.

For a gas that displays ideal behavior under isobaric conditions, the density (either mole density or weight density) at one temperature (D_{T1}) can be related to the density of the gas at a second temperature (D_{T2}) by the following expression:

$$D_{T2}/D_{T1} = T1/T2 \qquad (3)$$

Equation (3) represents an extremely simple relationship for describing isobaric atmospheric gas densities as functions of atmospheric temperature.

Schroeder and Munthe (1998) suggested an environmental tropospheric atmospheric temperature range of 40 °C to -60 °C as adequate for representing global temperature differences between tropical and polar regions. Using these temperature estimates, one also can predict an atmospheric isobaric mass density ratio of $D_{-60}/D_{40} = 1.47$. Given that atmospheric trace vapor concentrations are sometimes reported in raw units of mass density (e.g., nanograms or picograms per cubic meter), it is our hypothesis that the ideal gas component of the behavior of atmospheric trace gases also will lead to a number or mass density compression comparable to that of the major gases when tropical air masses are transported to polar regions. Consequently, in contrast to vapor concentrations reported in units of volume fractions, mole fractions, or mass/unit volume normalized to STP, trace vapor concentrations reported in raw units of mass/volume also will be sensitive to near surface tropospheric temperatures.

METHODS

Published data in the technical research literature were scrutinized for the purpose of estimating latitudinal tropospheric trace vapor concentration gradients for vapor phase concentrations of a number of species including: 1) elemental mercury (Slemr and Langer, 1992), 2) SF_6 (Geller et al., 1997), 3) POPs (persistent organic pollutants; Iwata et al., 1993; Schreitmuller et al., 1995; Lohman et al., 2001; Lukaschus et al., 2002) and 4) CFCs (Libo et al., 2001). All trace vapor concentration data were fitted to a 3rd order polynomial for the purpose of generating estimates of the ratio of observed vapor concentrations to those observed at the equator. When the data were published in graphical form, they were first digitized prior to being subjected to the fitting procedure.

Because reported vapor concentrations are frequently obtained from oceanic shipboard latitudinal transects, average January and July surface atmospheric temperatures were obtained from isotherms located at 20 degrees West longitude (in the Atlantic Ocean) from illustrations published in Berry et al. (1945).
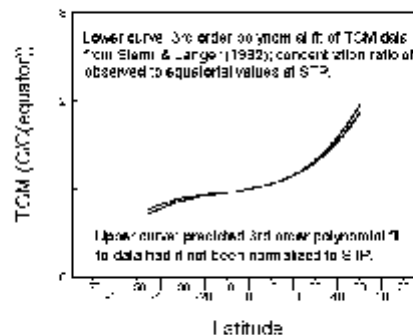

Fig. 1. Comparison of Total Gaseous Mercury concentration ratios at STP to predicted concentration ratios had the data not been normalized. Data from Slemr and Langer (1992).

RESULTS

The lower curve in Figure 1 illustrates the results of a 3rd order polynomial fit to mass-concentration-based ratios of total gaseous tropospheric mercury (TGM) based on data published by Slemr and Langer (1992). These authors normalized their results to STP and hence, this lower curve represents an actual latitudinal TGM gradient. The reader can observe a pronounced increase in this ratio with proximity to the pole in the northern hemisphere; this pattern is generally consistent with what was observed for most of the vapor data examined in this study. The upper curve in Figure 1 illustrates our predicted mass concentration ratio curve using a 3d order polynomial fit to published tropospheric temperatures in the Atlantic Ocean (Berry et al., 1945) based on the assumption that Slemr and Langer (1992) had reported their data in raw form (i.e., unnormalized to STP). The reader can observe a 5-10% difference between the two curves in regions distant from the equator.

The lower curve in Figure 2 illustrates volume fraction tropospheric SF_6 concentration ratios in the Atlantic Ocean derived from data published by Geller et al., 1997. Because this data was in units of volume fraction, this curve also is "real" and is likely consistent with Geller et
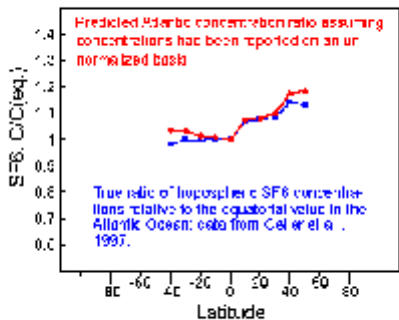
Fig. 2. Latitudinal tropospheric SF$_6$ concentration ratios estimated from published data. Lower curve represents volume fraction ratios; upper curve designates predicted ratios had data been reported on an unnormalized mass concentration basis. Data from Geller et al. (1997).

al.'s (1997) hypothesis that interhemispheric SF6 concentrations are limited by eddy dispersion between the two hemispheric air masses. The upper curve in Figure 2 illustrates predicted mass concentration ratios for SF6 using equation (3) and temperatures generated from the 3rd order polynomial fit to tropospheric temperatures in the Atlantic Ocean. The reader can easily discern that tropospheric temperature variations can significantly contribute to latitudinal vapor concentration gradients when concentration values are reported on an unnormalized mass density basis.

DISCUSSION

The data examined in this work strongly suggests that several concurrent processes are operative in the distribution of tropospheric trace gases. As a first approximation, none of these gases can be considered to be "inert" and hence, emission and/or loss rates are apparently faster than atmospheric inter-hemispheric mixing rates. As suggested by Geller et al. (1997), gases generated disproportionately in the northern hemisphere display a classical dispersive type profile limited by rates of dispersion between the two hemispheres.

The upper curves in Figures 1 and 2 suggest that at least part of the Northern Hemisphere latitudinal vapor concentration gradients observed in many studies reported in units of unnormalized mass concentration can be attributed to atmospheric density increases associated with cooling of these air masses as they are transported away from equatorial regions. Based on published estimates of equatorial and polar near-surface temperatures, one can plausibly suggest that a variation of as much as 50% of the equatorial value can be attributed to isobaric temperature-related volume contractions when data is reported on an unnormalized mass concentration basis. On this basis, variations between equatorial and polar vapor concentrations greater than 50% are required to generally indicate "real" changes in concentration.

This work has examined the role of tropospheric temperatures on unnormalized mass concentration based trace gas measurements. There are two other parameters that also may influence these values: 1) variations in atmospheric pressure and 2) variations in relative humidity. Tropospheric temperatures may lead to unnormalized mass concentration variations of as much as 50%. Surficial (coastal) air pressure variations of approximately 4% also have been reported in the technical literature (Petterson, 1956). Hence, one can anticipate a potential mass concentration variation of approximately 4% for data reported on an unnormalized mass concentration basis. As with tropospheric temperature variations, pressure variations will not alter concentrations reported in units of normalized mass concentration, mole fraction or volume fractions; however, the effects of tropospheric temperature variations are potentially more than 10 times greater than the effects of surficial pressure variations.

Assessing vapor concentration variations attributable to changes in relative humidity is more complicated. One reported saturation water vapor concentration at 40 degrees Celsius and at a pressure of one atmosphere was estimated to be 55.32 mm Hg or ~49 g/m^3. If one assumes that atmospheric water vapor concentrations range from 0 to the values given above, then the maximum concentration changes attributable to variations in relative humidity are: 7.3% on a partial pressure basis (100*55.32/760) and 3.8% on a mass fraction basis (100*49/1292). However, in contrast to variations in surficial tropospheric temperatures and pressures, variations in atmospheric water vapor concentrations will lead to commensurate variations in

trace gas concentrations reported in any of the units listed previously. Specifically, the addition of water vapor to the atmosphere will dilute trace gas concentrations and the loss of water vapor from the atmosphere will concentrate trace vapor concentrations (assuming that the trace vapors display conservative behavior). Alternatively, the effects of variations in surficial tropospheric temperatures are likely to be an order of magnitude greater than the effects of variations in atmospheric water vapor content with unnormalized data. Hence, the need to consider atmospheric water vapor concentrations will depend to a large degree on the requisite sensitivity of the modeling exercise.

One can also consider circumstances where conservative atmospheric trace aerosols are under investigation Clearly, mass concentration based aerosol measurements also would experience the same temperature dependent volume contraction phenomenon as do trace vapors reported on an unnormalized mass concentration basis. In contrast to trace vapors, atmospheric aerosols are relatively incompressible and hence, reporting these data on a volume fraction basis would not solve the problem of temperature dependence (even assuming that the density of the aerosols was known). We suggest that reporting tropospheric aerosol mass/volume data normalized to a reference temperature and pressure might be an appropriate method for comparing latitudinal aerosol concentration measurements.

CONCLUSIONS

The ideal gas model examined here is an extremely simple approach designed for estimating trace vapor concentrations for well mixed, refractory ideal gases that do not exhibit significant partitioning with either aquatic or terrestrial surfaces. No such ideal environmental vapor exists; however, the profiles illustrated in the results section strongly tend to suggest that there is a significant ideal gas component to published, unnormalized, latitudinal mass-concentration-based trace vapor gradients. Alternatively, vapor concentrations reported in units of mole fraction, partial pressure or mass concentration normalized to a reference temperature can provide insight into mechanisms influencing global vapor fate and transport. Lastly, variations in surficial tropospheric pressure and relative humidity also may be required in models designed for maximum accuracy.

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