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Effects of multi-media partitioning of chemicals on Junge's variability–lifetime relationship

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Abstract

Junge's variability–lifetime relationship describes the relation between the tropospheric residence time of a volatile trace gas and the coefficient of variation of the tropospheric mixing ratio at a remote location. However, no unique or universal quantification of this relationship exists. It can only be derived on a case-by-case basis for consistent data sets on substances with similar source and sink patterns. Using a multi-media model of the long-range transport of organic compounds, we determine variability–lifetime relationships for volatile substances. Next, we demonstrate how the variability–lifetime relationship can be obtained for semi-volatile organic compounds (SOCs) with the model and we investigate typical deviations from the Junge relationship for volatile compounds that are caused by the multi-media partitioning of SOCs. One cause of deviation from this relationship is substances undergoing significant transport in water so that their distribution in air is noticeably influenced by their distribution in water. The other, wider, deviation is caused by substances with a strong tendency for deposition and re-volatilization. Finally, we address the comparison of the model results with field data. Preliminary analyses of long-term monitoring data for polychlorinated biphenyls at remote sites have shown that the identification of Junge relationships in field data is not straightforward. We discuss possible strategies for the derivation of Junge relationships from field data on SOCs.

Keywords: Junge hypothesis; Multimedia models; Atmospheric lifetime; Atmospheric trace gases; Persistent organic pollutants

1. Introduction

The idea that the tropospheric distribution of a trace gas with a long residence time is more homogeneous than the distribution of a short-lived one is intuitive. An exact quantification of such a variability–lifetime relationship would be of great value to atmospheric chemistry because it would allow for the determination of tropospheric residence times based on the variability of trace gas concentrations or mixing ratios.

This idea has been explored both theoretically and empirically by Junge (1974). In his theoretical considerations, Junge (1974) identifies two main assumptions which are critical for a quantification of the variability–lifetime relationship. First, the standard deviation of the source distribution needs to be much larger than the standard deviation of the sink distribution. Second, the source and sink distributions of the different trace gases considered need to be similar. Junge (1974) determined the empirical relationship

$$\rho_x = a_{\mathrm{Junge}} \cdot t_{\mathrm{a}}^{-b_{\mathrm{Junge}}}, \tag{1}$$

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with $a_{\mathrm{Junge}}=0.14$ yr and $b_{\mathrm{Junge}}=1$. The coefficient of variability of the mixing ratio of a specific trace gas in the troposphere, ρ_x, is defined as the standard deviation divided by the mean of the sample used. t_a is the tropospheric residence time. The relationship is based on naturally occurring trace gases such as Rn, O_3, CH_4, CO_2, and O_2.

Besides this empirical result, a number of variability–lifetime relationships have been derived based on theoretical considerations (Gibbs and Slinn, 1973; Baker, 1979; Jaenicke, 1982; Slinn, 1988). These relationships generally have the form of Eq. (1), with b_{Junge} values between 0.5 and 1.0 (Table 1). In the works of Jaenicke (1982) and Slinn (1988), b_{Junge} depends on t_a, increasing from a value of 0.5 for small t_a to 1.0 for large t_a.

Using a vertical and latitudinal 2-D grid point model, Hamrud (1983) explored the dependence of a_{Junge} and b_{Junge} on different source and sink distributions, finding b_{Junge} values between 0.63 and 0.91.

A number of additional studies were published recently which are nearly all based on extensive data on trace gas mixing ratios (Colman et al., 1998; Ehhalt et al., 1998; Jobson et al., 1998, 1999; Williams et al., 2000; Johnston et al., 2002). Colman et al. (1998) used the variability–lifetime relationship of ethane and chlorinated 2-C hydrocarbons sampled over the South Pacific with a b_{Junge} value of 1.35 to determine the residence time of CH_3Br. Using a 3-D chemical tracer model (CTM) and hypothetical Rn-like tracers, Ehhalt et al. (1998) found that b_{Junge} takes a unique value in each grid cell, with values close to zero near sources and values close to 1.0 at remote locations.

Table 1
Values for exponents b in Eqs. (1) and (2), taken from the literature

Source	b_{Junge} or b_{Jobson}	Comment
Gibbs and Slinn (1973)	0.5	Theoretical
Junge (1974)	0.95	Theoretical
	1	Empirical, trace gases
Baker (1979)	0.5	Theoretical
Jaenicke (1982)	0.5–1	Theoretical
	0.5	Low t_a
	1.0	High t_a
Hamrud (1983)	0.63–0.91	2-D model
Slinn (1988)	0.5–1	Like Jaenicke (1982), with transport
Jobson et al. (1998)	0.28–0.56	Empirical
Colman et al. (1998)	1.35	Empirical
Ehhalt et al. (1998)	0.5	Empirical
	0–1	3D-CTM
Jobson et al. (1999)	0–1	Empirical
	0.18	Near source
	≈0.5	Troposphere
	≈1.0	Stratosphere
Williams et al. (2000)	0.64	Empirical
Johnston et al. (2002)	0.57–0.98	3-D CTM
	1.72	Empirical
Lenschow and Gurarie (2002)	0.5–1.0	1-D vertical model

CTM: chemical tracer model.

Jobson et al. (1998) presented an elegant theoretical derivation of the variability–lifetime relationship, formulated as

$$\sigma_{\ln x} = \sigma_t \cdot t_\mathrm{a}^{-b_{\mathrm{Jobson}}}, \tag{2}$$

with $b_{\mathrm{Jobson}}=1$, which is considered as a theoretical upper limit (Jobson et al., 1998). $\sigma_{\ln x}$ is the standard deviation of the natural logarithm of the measured mixing ratios, x. σ_t is the standard deviation of the travelling times from the source to the point of sampling needed by the air parcels that correspond to the measured mixing ratios, x. Junge's and Jobson's variability–lifetime relationships are equivalent for specific average values of the measured mixing ratios. Jobson et al. (1998) and Jobson et al. (1999) analyze a number of data sets sampled at different locations and find b_{Jobson} values around 0 for locations near sources, values of about 0.5 for sampling in the free troposphere and values near 1.0 for sampling in the stratosphere.

Williams et al. (2000) explored different variability–lifetime relationships in samples taken in Surinam which they explained by the different sources of the substances investigated. Lenschow and Gurarie (2002) used a theoretical vertical 1-D model to find variations of the variability–lifetime relationship depending on altitude, from the planetary boundary layer up to the stratosphere. Both studies illustrate the numerous contexts in which differing variability–lifetime relationships are obtained.

Johnston et al. (2002) returned to the original purpose of the variability–lifetime relationship, which is the determination of atmospheric residence times based on measurements of the variability of the substances concerned. In their critical discussion, they point out the large uncertainty of t_a values determined from a variability–lifetime relationship. Using a 3-D CTM and investigating the effect of different sink types on the resulting ρ_x values, they quantify the uncertainty caused by this variability alone as ±20%.

The conclusion drawn by Johnston et al. (2002) can well serve as a summary of the research on the variability–lifetime relationship until now: "The variability–lifetime relation is not universal or unique and should be used only to compare consistent data sets for gases with similar source and sink patterns." In particular, the value of b_{Junge} varies considerably and is close