STANDARD ERROR CALCULATIONS FOR NON-SEASALT CONSTITUENTS IN MARINE PRECIPITATION

MARK E. HAWLEY*, JAMES N. GALLOWAY, and WILLIAM C. KEENE

Department of Environmental Sciences, University of Virginia, Charlottesville, VA 22903, U.S.A.

Abstract. Pollutant transport studies and investigations of geochemical cycling often involve calculation of excess (non-seasalt) concentrations for various ions found in precipitation. Excess concentrations are calculated from measurements of the concentrations of a reference species and the species of interest. Formulas for determining the accuracy of calculated excess concentrations are necessary because this accuracy can vary significantly from sample to sample within the same data set, as well as from one study to another. The formulas derived in this paper demonstrate that the standard error of calculated excess concentrations is dependent on the nature and magnitude of the analytical errors made in measuring total concentrations. Application to a real data set indicates that this standard error is often greater than the calculated excess concentration, and that the standard error may vary by orders of magnitude for various samples in the same data set. The magnitude of the potential errors has important implications for the reliability of conclusions based on calculated excess concentrations, while the sample-to-sample variation of these errors complicates the process of determining the accuracy of summary statistics such as the volume-weighted mean concentration. In addition, these variations in accuracy can obscure the relationships between excess concentrations and other variables, both chemical and meteorological. This complicates investigations of source-receptor relationships and geochemical cycling, and may lead to faulty conclusions.

1. Introduction

The chemical composition of the marine atmosphere is influenced by a variety of sources in the terrestrial and marine environment. Some important atmospheric constituents, such as S, are contributed by many sources; determination of the proportions of total concentration contributed by each source is necessary for quantification of various geochemical cycles. Separation of marine and non-marine contributions can be accomplished by measuring the total concentration of the element in question and also the concentration of a reference element that is derived only from seawater. The excess (or non-seasalt) contribution can then be calculated as

$$[I]_E = [I]_T - [I]_{SS},$$ (1)

where $[I]$ represents the concentration of the species of interest and the subscripts E, T, and SS identify the excess, total, and seasalt-derived contributions, respectively. Assuming no fractionation of preferential scavenging, the seasalt contribution is calculated as

$$[I]_{SS} = K[R]$$ (2)

in which $[R]$ represents the total concentration of a reference species and K represents the sea water ratio of the concentrations of species I and R. This calculation also

---

* Author for all correspondence.

requires the assumption that all of the reference species originates from seawater and that there is no enrichment or depletion of the reference species in the atmosphere.

Because the excess portion of the species of interest is calculated as the difference between two measurements that are subject to significant analytical error, the calculated excess concentration is also subject to error. The accuracy of calculated excess concentrations of various ions in precipitation should be considered in drawing conclusions regarding source regions and geochemical cycles, especially from small numbers of samples. When many samples are available, summary statistics such as the volume-weighted mean concentration are reasonably accurate, even if the individual sample concentrations are subject to significant errors. However, for data sets in which the reliability of individual calculated excess concentrations is generally large and may vary significantly from sample to sample, determining the accuracy of the summary statistics is not straightforward. Furthermore, some of the calculated concentrations may be so inaccurate as to obscure the relationships between excess concentrations and other variables, both chemical and meteorological. Therefore, variations in the accuracy of calculated excess concentrations should be quantified and considered in studies of the chemistry of marine precipitation.

Keene *et al.* (1986), using data from precipitation collected at three marine locations, have discussed uncertainties in the calculation of non-seasalt components and tested the validity of assumptions involved in the use of sea-salt corrections. They assessed the importance of small differences between the ratios of reference species in precipitation, compared to those of seawater, for studies of tropospheric/biogeochemical cycles in general and marine precipitation chemistry in particular. In their conclusions, they recommend objective criteria for the calculation of sea-salt components.

This paper provides methods for determining the standard error of calculated excess concentration values. The standard error is a measure of the accuracy of the calculated excess concentration. Calculation of this measure of accuracy for a single observation is discussed, and formulas suitable for use with both relative and absolute analytical uncertainties are developed. These formulas are then applied to the problem of estimating the standard error of the volume-weighted mean concentration.

2. Methods

Equation (1) provides a method for estimating the excess concentration for a single sample. Under the assumption that the conservative reference species (R) is contributed exclusively by sea salt, and in the absence of fractionation and differential scavenging (which we postulate), $[I]_E$ is an unbiased estimator of the corresponding excess concentration. The total accuracy of an unbiased estimator can be characterized by its variance, which is a measure of the random or non-systematic error of the estimation procedure. In this paper, we will develop formulas for determining the variance $[I]_E$ under a variety of conditions. In applying these formulas to a real data set, we will characterize the accuracy of $[I]_E$ by the standard error, which is equal to the square root of the variance for this unbiased estimator.

Given a single sample for analysis, the question that must be addressed is, how accurately can the excess concentration of species I be determined? The excess concentration is calculated as

$$[I]_E = [I]_T - K[R],$$ (3)

where $[I]_T$ and $[R]$ are measured analytically. Errors in these analytical measurements will lead to errors in the calculated excess concentration. The seawater ratio, K, is a constant; appropriate values for some important ions are provided by Keene *et al.* (1986).

Taking the variance of both sides of Equation (3) leads to the formula

$$\text{var}[I]_E = \text{var}[I]_T + K^2 \text{var}[R] - 2 \text{cov}([I]_T, K[R])$$ (4)

in which var represents the variance of a random variable and $\text{cov}(\_\_, \_\_)$ indicates the covariance of two random variables. The concentration measurements $[I]_T$ and $[R]$ are treated as random variables to reflect the potential for measurement error. The sea-salt ratio, K, is treated as a known constant.

In order to apply Equation (4), the individual terms must be evaluated. Factors to be considered in this evaluation include the possibility of covariance, the nature of the analytical errors, and the effects of dilution and contamination.

2.1. IMPORTANCE OF THE COVARIANCE TERM

The covariance term in Equation (4) can be ignored in determining the standard error of estimate for a single calculated excess concentration because the errors of measurement for $[I]_T$ and $[R]$ are independent. The measured values of $[I]_T$ and $[R]$ can be decomposed into the true value of each and a measurement error:

$$\text{cov}([I]_T, K[R]) = \text{cov}\{([I]_T^* + \Delta_I), K([R]^* + \Delta_R)\}$$ (5)

in which the asterisks indicate the true (unknown) concentration values and Δ_I and Δ_R represent the measurement errors. Because the true values are constants, Equation (5) reduces to

$$\text{cov}([I]_T, K[R]) = \text{cov}(\Delta_I, K\Delta_R)$$ (6)

which holds even if the measurement methods are biased. As long as the analyses of $[R]$ and $[I]_T$ are made on separate aliquots of a well-mixed and uncontaminated sample, the covariance of the measurement errors should be zero. This argument applies only to the case of measurement error in a single sample; within a larger data set, the covariance of concentrations of various ions may be significantly different from zero.

2.2. ABSOLUTE VS RELATIVE ANALYTICAL PRECISION

The precision of laboratory techniques for measuring concentration values determines the variance of the measured concentrations, $[I]_T$ and $[R]$. This precision can be estimated by making repeated measurements on samples or standard solutions. In some cases, the precision (which is represented by the standard deviation of the measured

values) is nearly constant over the full range of concentration values; this is referred to as absolute analytical precision. In other cases, the precision varies with the actual concentration, most frequently as a near-constant percentage; this is referred to as relative analytical precision. The nature and level of precision for the particular analytical techniques being employed must be determined in order to use the formulas presented in this paper.

The concentration variance terms in Equation (4) are estimated as the square of the standard error of the analytical technique. If the precision of the analytical technique is nearly constant (absolute), then the concentration variance can be written as

$$\text{var}[I] = A_I^2 , \tag{7}$$

where A_I represents the absolute standard error in appropriate concentration units. For relative analytical precision, the variance is expressed as

$$\text{var}[I] = C_I^2[I]^2 , \tag{8}$$

where C_I represents the percentage of relative error. Thus, for the absolute precision case, Equation (4) becomes

$$\text{var}[I]_E = A_I^2 + K^2 A_R^2 , \tag{9}$$

where A_R is the absolute standard error for the reference species, R. For the relative precision case, the corresponding formula is

$$\text{var}[I]_E = C_I^2[I]_T^2 + K^2 C_R^2[R]^2 . \tag{10}$$

Because different analytical techniques may be used for different ions, it is also possible to have relative precision for one ion and absolute precision for the other in applying Equation (4).

2.3. EFFECTS OF SAMPLE DILUTION

Many of the analytical techniques used in studies of precipitation chemistry are only reliable over a limited range of concentrations. Because the observed concentrations of some of the important ions in marine precipitation (e.g., Na) vary over ranges considerably greater than the ranges of accuracy for the analytical methods, dilution is often necessary to bring the sample concentrations into the desirable range.

When the concentration of an ion is determined by analyzing a diluted sample, the concentration value is determined by multiplying the value measured on the diluted aliquot by the dilution factor. The dilution factor is simply the ratio of the volume of the diluted sample to the original sample volume. Thus we can write

$$[I]_T = D_I[I]_d , \tag{11}$$

where D_I represents the dilution factor and the 'd' subscript represents the concentration measured on the diluted aliquot.

If the standard error of the analytical technique used for an ion is absolute over the measurement range, multiplication by the dilution factor will affect the standard error

of the concentration value. For instance, suppose that the absolute standard error is 2.0 μeq L^{-1} over a concentration range of 0 to 500 μeq L^{-1}. The variance of $[I]_T$ would be equal to the square of this standard error, or 4.0 (μeq L^{-1})^2. If the value of $[I]_T$ was measured at 64.0 μeq L^{-1} on an aliquot that had been diluted by a factr of five, the value of $[I]_T$ would be obtained (using Equation (11)) as being 320 μeq L^{-1}. The variance of $[I]_T$ would be determined by

$$\text{var}[I]_T = \text{var}(D_I[I]_d) = D_I^2 \, \text{var}[I]_d = D_I^2 A_I^2 \tag{12}$$

which in this case would give a value of 100.0 (μeq L^{-1})^2. An analogous formula can be developed for the reference species. Therefore, if the precision of the analytical technique is absolute for both ions, and both concentrations are measured on diluted aliquots, Equation (9) becomes

$$\text{var}[I]_E = D_I^2 A_I^2 + K^2 D_R^2 A_R^2 . \tag{13}$$

This equation is valid if the dilution factors (D_I and D_R) and the seawater ratio (K) are treated as known constants.

If the standard error of the analytical techniques is relative (i.e., is a constant percentage of concentration), the magnitude of the dilution factor does not affect the variance or standard error of the concentration value. This is demonstrated by combining Equations (8) and (11);

$$\text{var}[I]_T = \text{var}(D_I[I]_d) = (C_I D_I[I]_d)^2 = C_I^2[I]_T^2 . \tag{14}$$

Again, an analogous formula can be written for the reference species, so Equation (10) is not affected by dilution of the samples if the dilution factors are treated as known constants.

2.4. EFFECTS OF CONTAMINATION AND ERRORS IN DILUTION

In calculating the standard error of measured values determined by analysis of diluted samples, the accuracy of the dilutions should be considered. Under routine laboratory conditions, dilutions are expected to be accurate to about $\pm 1\%$ (Keene and Pszenny, 1986). Mathematical analysis indicates that the effects of these measurement errors are typically insignificant when compared to the uncertainty of chemical concentration measurements. Therefore, the practice of treating the dilution factors as known constants is reasonable when the accuracy of volume measurements made in the process of sample dilution is $\pm 1\%$ or less.

The fact that a sample has been diluted before analysis should not be ignored entirely in evaluating the accuracy of derived excess concentrations because of the possibility of contamination. Although the likelihood of contamination during dilution is not high, the consequences may be very large due to the generally low concentrations of the ions of interest. Contamination will generally lead to overestimation of the actual concentrations of certain ions, most likely sodium and chloride if due to contact with the lab analyst's hands. An overestimation of the true Na concentration will lead to an underestimation of the excess concentration of other ions if Na is used as the reference species.

One possible manifestation of contamination during dilution or analysis is a negative excess concentration. This may occur if the measured concentration of Na is higher than the true concentration (due to contamination). Another likely result of contamination is a charge imbalance. Although these anomalies may be indicative of contamination during dilution or analysis, the variation in the magnitude and nature of the effects of contamination precludes the development of a variance formula that reflects this possibility.

3. Results and Discussion

The formulas developed in the preceding section indicate that the variance of a calculated excess concentration is a function of the dilution factors, the seawater ratio, and the analytical precision of laboratory techniques. Because these factors may vary from sample to sample, the standard error of the calculated excess concentration is variable. The behavior of this standard error is described in this section, along with an analysis of the effects of its variation in larger data sets. Application of the formulas to actual precipitation samples is included.

3.1. BEHAVIOR OF THE STANDARD ERROR

Equations (10) and (13) can be used to determine the variance of the calculated excess concentration for a single sample. The standard error of $[I]_E$ is equal to the square root of this variance because $[I]_E$ is an unbiased estimator under the assumptions on which these equations are based.

The variation of the standard error of $[I]_E$ as a function of the total and excess concentrations of the species of interest is illustrated in Figures 1 through 4. Specifying values of the total and excess concentrations determines the concentration of the reference species for any particular pair of ions, I and R, because the seawater ratio (K) is fixed. For purposes of illustration, these figures were constructed using sulfate (SO_4) as the species of interest with Na as the reference species. The seawater ratio ($\mu eq/\mu eq$) for this pair of ions is given by Keene et al. (1986) as 0.121. In our laboratory, the usual measurement scale for SO_4 in marine precipitation is 0 to 14 $\mu eq\ L^{-1}$, which corresponds to (0 to 5 mg L^{-1}); for Na, the measurement scale is 0 to 87 $\mu eq\ L^{-1}$, or (0 to 2 mg L^{-1}). When higher concentrations are encountered, sample aliquots are diluted by factors of 3, 5, 10, or 20 to 1 to bring the concentration into the desired range for measurement. The regions labeled as impossible in the figures represent situations in which the excess concentration is greater than the total concentration for the species of interest. The range of values used in the figures corresponds to the range of data found in samples collected at the Harbor Radio Tower site on Bermuda; ranges for other sites and pairs of ions may differ considerably from those used here.

3.1.1. *The Absolute Precision Case*

If both ions are measured with absolute precision, the variance of $[I]_E$ is calculated with Equation (13), and the standard error is expressed as

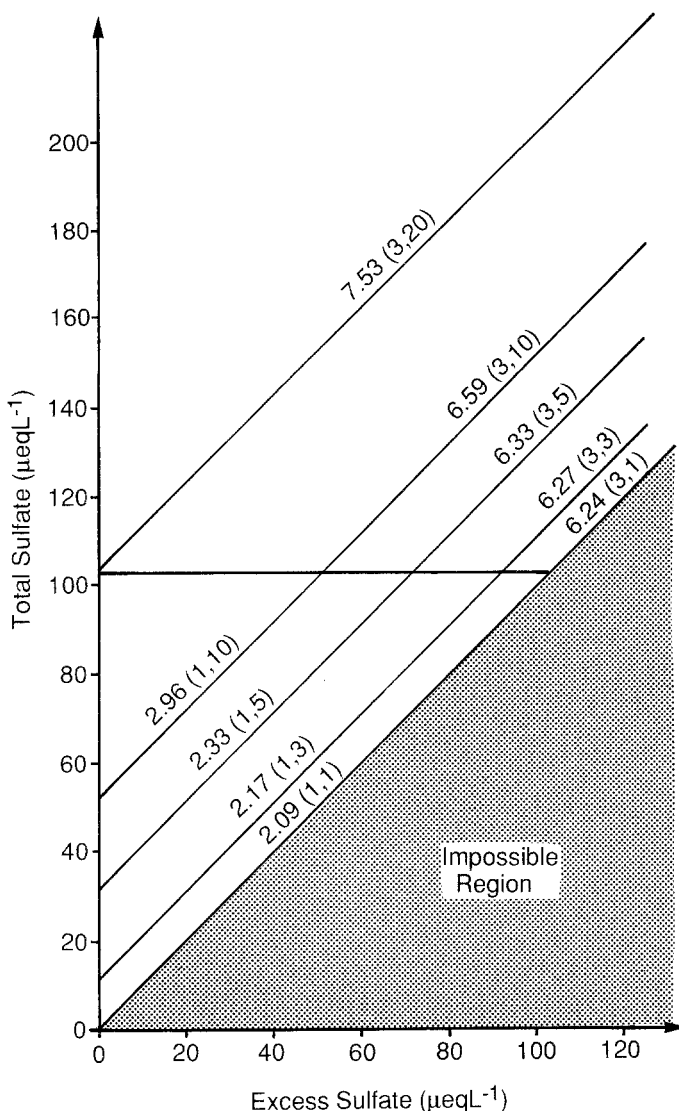$$\text{Standard error } [I]_E = (D_I^2 A_I^2 + K^2 D_R^2 A_R^2)^{1/2} . \tag{15}$$

Fig. 1. Standard error ($\mu eq\ L^{-1}$) of excess concentrations calculated from measurements made with absolute analytical errors of 2%; values in parentheses are dilution ratios (D_I, D_R) and define regions of constant standard error.

Assuming an absolute analytical error equal to 2% of the measurement scale for each ion leads to values of A of 2.08 and 1.74 $\mu eq\ L^{-1}$ for SO_4 and Na, respectively.

Figure 1 demonstrates that the standard error of $[I]_E$ varies considerably over a relatively narrow range of concentration values. In addition, this variation is discrete, rather than continuous, because the standard error is a function of the dilution factors but is otherwise independent of the total and excess concentrations. High standard errors are not associated exclusively with high values of $[I]_E$; an SO_4 concentration of 10 $\mu eq\ L^{-1}$ may be subject to a standard error as low as 2.09 or as high as 7.53 $\mu eq\ L^{-1}$.

If the standard error of $[I]_E$ is expressed as a percentage of the calculated value, the variation is continuous within dilution regions but discontinuous across regional boundaries. This behavior is illustrated in Figure 2. If an excess SO_4 concentration of 40 μeq L^{-1} is calculated from a sample with 100 μeq L^{-1} of SO_4, the standard error of $[I]_E$ would be 2.96, or about 7.4%; but if the same excess concentration was determined for a sample with 110 μeq L^{-1} total SO_4, the standard error would be 6.59, or about 16.5%. Thus, the reliability of individual calculated excess concentrations should not be treated as a constant quantity, nor as a constant percentage of $[I]_E$.

Fig. 2. Relative standard error (% of $[I]_E$) of excess concentrations calculated from measurements made with absolute analytical errors of 2%: values in parentheses are dilution ratios (D_I, D_R); dashed lines are isoplets of equal percentage error.

3.1.2. *The Relative Precision Case*

In situations where both species are measured with relative analytical precision, the standard error formula is

$$\text{Standard error}\,[I]_E = (C_I^2[I]_T^2 + K^2 C_R^2[R]^2)^{1/2}. \tag{16}$$

In this case, the standard error is independent of the dilution factors and dependent on the measured concentrations. Figure 3 illustrates the behavior of the standard error of $[I]_E$ if both species are measured with a relative analytical precision of $\pm 5\%$ of their
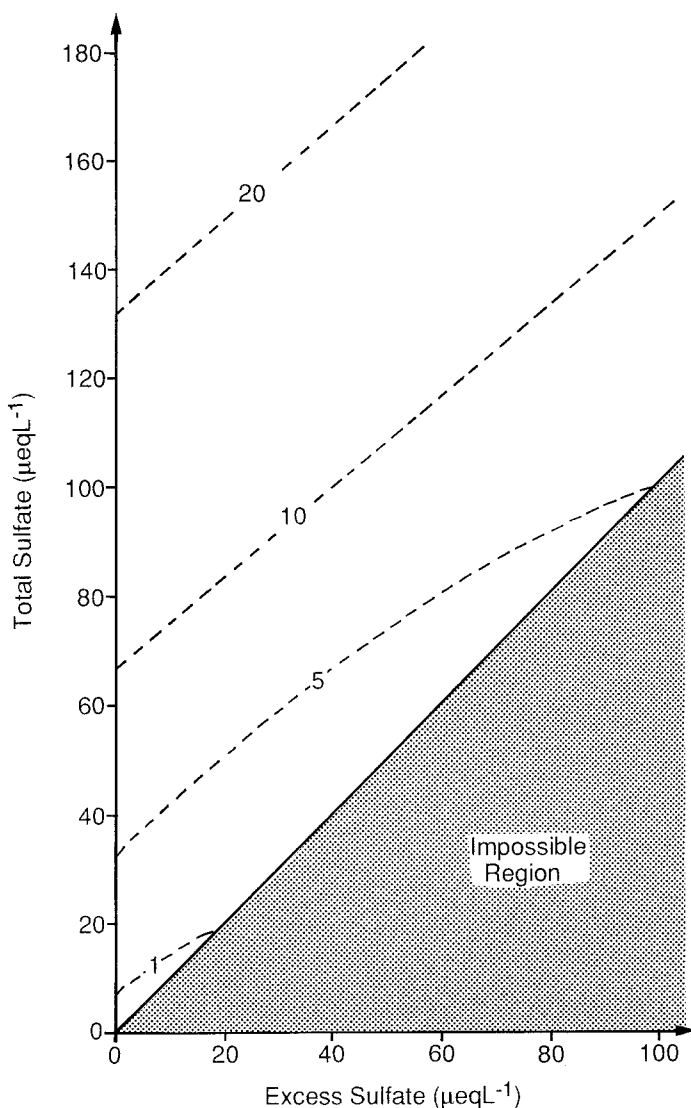

Fig. 3.   Absolute standard error (μeq L^{-1}) of excess concentrations calculated from measurements made with relative analytical errors of 5%; dashed lines are isopleths of equal error.

MARK E. HAWLEY ET AL.

measured values. The standard error varies continuously and over a larger range than in the corresponding diagram for the absolute precision case (Figure 1). Again, knowledge of the calculated excess sulfate concentration is not sufficient to determine the standard error of the calculated value; a calculated excess concentration of 10 μeq L^{-1} may have a standard error of less than one to greater than 20 μeq L^{-1}. Figure 4 shows that when the standard error is expressed as a percentage of the excess concentration, low excess concentration values tend to be less precise.
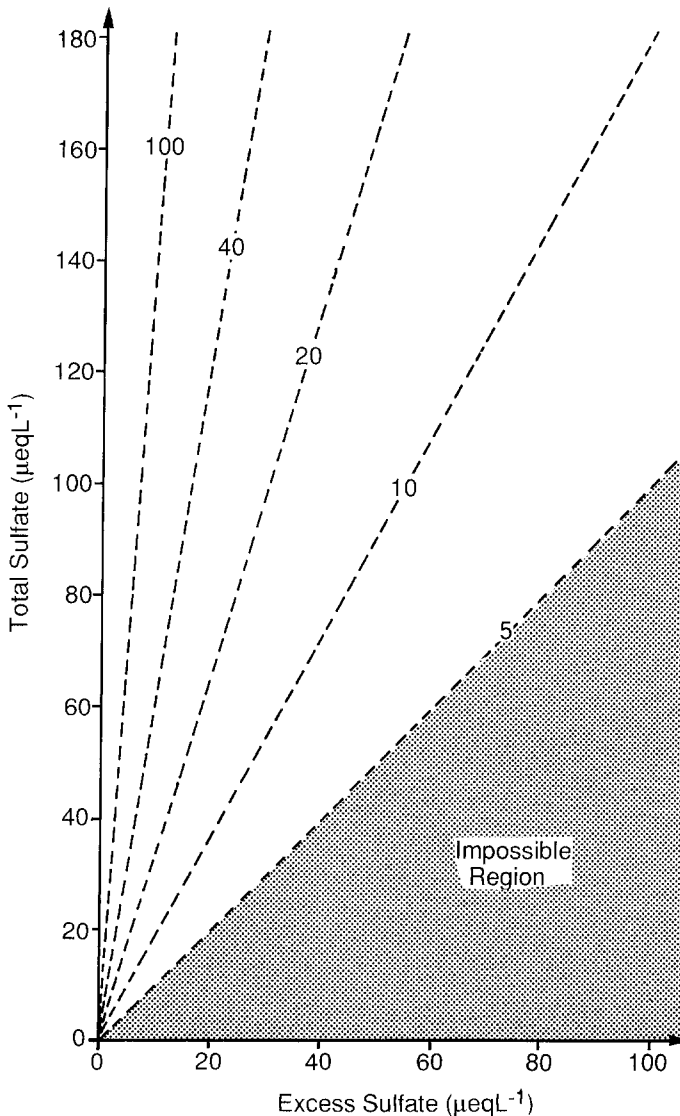

Fig. 4.   Relative standard error (% of $[I]_E$) of excess concentrations calculated from measurements made with relative analytical errors of 5%; dashed lines are isopleths of equal percentage error.

3.1.3. *Other Cases*

In an actual experiment where the excess concentration is to be determined, circumstances may be different from those described in the preceding sections. For instance, one of the ions may be measured with absolute precision and the other with relative precision. Another possibility is that the analytical precision for a single ion may be absolute at very low concentrations (reflecting a minimum detection level) and relative at higher concentrations; even within the range of concentrations where the analytical technique is accurate, the nature of the precision may vary. Each laboratory should evaluate the nature and level of analytical precision for each species empirically.

In light of all the factors involved in defining the circumstances under which the excess concentration will be calculated, it is not feasible to present figures or equations for all possible cases. However, the equations provided in this paper can be combined and adapted to determine the accuracy of calculated excess concentrations for any particular set of circumstances. Figures 1 through 4 illustrate the nature of the relationships between the error of the calculated excess, the measured concentrations, and the analytical precision of the measurement techniques for two specific scenarios.

3.1.4. *Harbor Radio Tower Data*

The importance of knowing the nature and magnitude of the analytical errors is illustrated by Table I. The standard errors for a few of the 127 observations collected at the Harbor Radio Tower site on Bermuda are presented for three different error scenarios. These observations were selected to represent the range of dilution ratios and excess sulfate concentrations encountered in this data set. The results illustrate the fact that an incorrect assumption regarding the analytical errors can lead to large errors in estimating the reliability of calculated excess concentrations, and also that the standard error is not a simple function of excess concentration.

TABLE I

Standard error[a] for calculated excess sulfate concentrations at Harbor Radio Tower, Bermuda

Concentrations (μeq L^{-1})			Dilution ratios		Analytical error scenario		
$[Na^+]$	$[SO_4]_T$	$[SO_4]_E$	D_I	D_R	Absolute @ 2% of range	Relative @ 5% of value	Relative @ 10% of value
60.98	14.45	7.070	1	1	2.09 (29.6)	0.81 (11.5)	1.62 (22.9)
126.8	24.71	9.372	1	3	2.17 (23.2)	1.45 (15.5)	2.91 (31.0)
358.4	63.46	20.1	1	5	2.33 (11.6)	3.84 (19.1)	7.70 (38.3)
440.8	54.78	1.436	1	10	2.96 (206.)	3.82 (266.)	7.64 (532)
695.9	106.0	21.81	3	10	6.59 (30.2)	6.76 (31.0)	13.5 (62.1)
1071.	174.7	45.09	3	20	7.53 (16.7)	10.9 (2.41)	21.7 (48.2)
96.00	12.53	0.918	1	3	2.17 (236.)	0.85 (93.1)	1.71 (186.)
175.7	87.11	65.85	1	3	2.17 (3.30)	4.48 (6.81)	8.97 (13.6)

[a] Expressed in μeq L^{-1} and (in parentheses) as a percentage of the corresponding excess sulfate concentration.

3.2. IMPLICATIONS FOR LARGER DATA SETS

The major implication of the preceding analysis is that the accuracy of calculated excess concentrations may vary considerably from one observation to the next, as well as from ion to ion for the same water sample. Thus, if one compiles a set of excess concentration values (either for a number of different observations or a number of different ions), the resulting data set is not composed of equally reliable values. This can be of major consequence in any further analyses.

3.2.1. *Complete vs Representative Sampling*

For the following discussion, it is important to note the differences between two types of analysis that may involve sets of concentration values. In the first type, the concentration is measured or calculated for each event in the population of interest; this is the complete sampling situation. An example might be a study in which a mass balance for sulfate is prepared for a particular time period and location. If the data set includes precipitation samples for each rainfall event that occurred during the specified time period, the situation is one of complete sampling of the population of interest.

In the other case, the available data are considered to be a representative subset (or sample) of a larger population. For instance, if we have obtained precipitation samples for one storm in each month at a particular location for the last 24 mo, the resulting data might be considered to be a representative sampling of the population of all storm events that occurred during that period. If one postulates that the events of the last 2 yr are representative of some larger time domain, or that the particular measurement site is representative of a larger area, statistical methods can be used to draw inferences about larger populations from the available data set.

In the complete sampling case, the accuracy of the individual event concentration values determines the error with which the population characteristics can be calculated; the error in the calculated population values arises solely from measurement errors. In the second case, values of the population characteristics must be inferred rather than calculated directly from the sample values. This inference is based on the assumption that the available values form a representative subset of the population. The inference process is a source of additional uncertainty in estimating the population characteristics. In this paper, we will address the complete sampling situation only.

3.2.2. *Application to Volume-Weighted Means*

Spatial and temporal variations in precipitation chemistry are frequently studied by comparisons of volume-weighted mean concentrations (e.g., Galloway *et al.*, 1984). The volume-weighted mean concentration (VWMC) can be calculated from chemical analyses of precipitation samples from n storm events as

$$\text{VWMC} = (\Sigma v_i c_i)/(\Sigma v_i), \tag{17}$$

where v_i is the volume (depth) of rainfall and c_i is the measured concentration of a specific ion of interest for event i.

In order to draw reliable conclusions from comparisons of VWMC's, it is necessary to consider the reliability of each VWMC being compared. The reliability of a VWMC can be quantified by the standard error of the calculated VWMC as an estimator of the true (unknown) VWMC for the n available precipitation samples; this represents the accuracy of the VWMC in the complete sampling case.

If one assumes that the depth of rainfall for each sampled event is determined without error, then the only source of differences between the true VWMC and the calculated value is analytical error in determining the individual concentration values. Assuming that the analytical techniques are unbiased, the calculated VWMC is an unbiased estimator of the true VWMC, and the standard error of the calculated value is equal to the square root of its variance. If the observed events are independent (i.e., there is no event-to-event autocorrelation in the concentration values), the variance of the VWMC can be calculated as

$$\text{var}(\text{VWMC}) = \sum (v_i/\Sigma v_i)^2 \, \text{var}(c_i) \,. \tag{18}$$

The variance of the concentration terms in Equation (18) should be calculated using formulas that reflect the precision of the chemical analyses. The reliability of the sample VWMC as an estimator of the corresponding population value has been discussed elsewhere (e.g., Miller, 1974; Liljestrand and Morgan, 1979; Hawley, 1985), and formulas for this purpose (i.e., for use in the representative sample situation) are not appropriate for use when all of the events in the population of interest have been observed.

The fact that concentrations determined for individual events are of variable accuracy means that the variance of the concentration terms in Equation (18) is not a constant. Therefore, the approach of computing the variance of the available concentration values and using this to represent the variance of each value is not appropriate. If this were done, Equation (18) could be re-written as

$$\text{var}(\text{VWMC}) = \text{var}(c) \sum (v_i/\Sigma v_i)^2 \,. \tag{19}$$

This formula is based on the assumption that the available concentration values are samples drawn from a homogeneous population and all have the same variance. In general, this is not true in precipitation chemistry. If the measurement errors are relative, the variance of each observation is a function of the true concentration, which undoubtedly varies from sample to sample. If the measurement errors are absolute, the variance of each observation is a function of the dilution factors. If no dilutions are necessary, the variances of the observations are equal. However, even if the variances are equal, the expected concentration of most species is determined in part by the volume of rainfall, which varies from one storm event to the next. Therefore, the assumption that all observed concentrations are identically distributed is not generally valid, and use of Equation (19) will result in overestimation of the standard error of the sample VWMC.

Table II illustrates the accuracy of the VWMC for various analytical error situations, formulas, and numbers of storm events. The standard error of the VWMC is expressed

TABLE II

Standard error[a] of calculated volume-weighted mean sulfate concentrations at Harbor Radio Tower, Bermuda

Analytical error scenario	Total sulfate (VWMC = 26.239)			Excess sulfate (VWMC = 13.588)		
	Formulas for calculation of standard error	Sample size		Formulas for calculation of standard error	Sample size	
		$n = 10$	$n = 127$		$n = 10$	$n = 127$
Absolute @ 2% of analytical range	12, 18	0.963 (3.67)	0.255 (0.97)	15, 18	1.06 (7.79)	0.265 (1.95)
Relative @ 5% of measured concentration	14, 18	0.544 (2.11)	0.173 (0.66)	16, 18	0.707 (5.20)	0.198 (1.46)
Relative @ 10% of measured concentration	14, 18	0.997 (3.80)	0.346 (1.32)	16, 18	1.40 (10.3)	0.395 (2.91)
Not considered: variance calculated from observed values	19	9.16 (34.9)	3.38 (12.9)	19	5.60 (41.2)	1.62 (11.9)

[a] Expressed in μeq L^{-1} and (in parentheses) as percentage of the corresponding volume-weighted mean concentration (VWMC).
n = number of observations used in calculating the VWMC.

as a percentage of the VWMC for total and excess sulfate concentrations determined for storm events at the Harbor Radio Tower site on Bermuda. The implications of the numbers in Table II are:

(1) use of Equation (19) (i.e., the treatment of the observations as identically distributed random variables) leads to considerable overestimation of the true standard error of the VWMC and to the erroneous conclusion that the excess VWMC is more accurate than the total VWMC;

(2) correct estimation of the standard error of the VWMC requires a knowledge of the nature and magnitude of the errors in the chemical analysis, and may also require a knowledge of any dilutions performed as part of this analysis;

(3) the magnitude of the standard error is affected by the number of observations (samples) for which the VWMC is calculated; and

(4) the relative (percent) standard error of the calculated excess VWMC is significantly larger than that of the VWMC of the measured total concentrations.

The precision of the VWMC in the case of complete enumeration is generally quite good, especially for large sample sizes. Even with small sample sizes and large analytical errors, the standard error of the excess sulfate VWMC is just over 10% of the calculated value, or less than 1.5μeq L^{-1}. However, the excess VWMC is much less reliable than the total VWMC, even with large sample sizes and small analytical errors. The accuracy of the VWMC improves as the number of observations increases due to the fact that each additional observation reduces the weights of all the other observations and the sum of the squares of the weights in Equation (18) is also reduced. In addition, storm events with high variances for the calculated excess sulfate concentration tend to be those with high total sulfate concentration, and these events tend to have small rainfall

volumes. Therefore, the high-variance events tend to have relatively low weights when Equation (18) is used to determine the variance of the VWMC.

3.2.3. *Implications for Cycling and Transport Studies*

The effects of sample-to-sample variation in the accuracy of calculated excess concentrations are not limited to the VWMC. These variations should be recognized and accounted for in determining the accuracy of any other summary statistics (e.g., the arithmetic mean), and also in more detailed investigations of geochemical cycling.

As an example, suppose that a data set consisting of concentration measurements and back-calculated air mass trajectories was available for investigation of source-receptor relationships. The calculated excess concentration values are reasonably accurate for some species and storm events; but for some others, the standard error is larger than the calculated value. If all calculated concentrations are treated as equally accurate, the large random errors associated with the less reliable excess concentrations may mask an otherwise clear relationship between trajectory and the excess concentration of a certain species. Determination of the standard errors for calculated excess concentrations of various ions may also be helpful in understanding the rates at which chemical reactions occur in the atmosphere.

5. Conclusions

The formulas developed for the case of a single observation indicate that the standard error of the calculated excess concentration is determined by the nature (relative vs absolute) and the magnitude of the analytical errors for the reference species and the species of interest. In the absolute error case, dilutions must be accounted for, and the standard error varies discretely as a function of dilution factors. In the relative error case, the standard error varies continuously as a function of the measured concentrations. For individual observations, the standard error can be much greater than the calculated excess concentration. The standard error tends to be higher for events with large sea-salt components and low excess concentrations.

When groups of observations are used to calculate summary statistics, such as a volume-weighted mean excess concentration, care must be taken in evaluating the accuracy of these statistics because the accuracy of the individual excess concentrations may vary from one observation to the next. The standard error of the volume-weighted mean excess concentration decreases as the number of observations increases, and is generally significantly larger than the corresponding standard error for the total concentration of the species of interest.

This analysis has important implications for investigations of the composition of the marine atmosphere and precipitation. When excess concentrations from individual events are used (e.g., when excess sulfate data are used to estimate atmospheric transformation reactions) the uncertainty introduced in calculating the excess concentration as a difference of two measured concentrations can be very large, and may vary considerably from sample to sample. However, when volume-weighted means for

complete data sets of excess components are used to draw conclusions about biogeochemical cycles, the relative errors are smaller and decrease rapidly as the size of the data set increases. The sample-to-sample variation in accuracy may obscure the relationships between excess concentrations and other chemical and meteorological variables, thus complicating the interpretation of larger data sets.

References

Galloway, J. N., Likens, G. E., and Hawley, M. E.: 1984, *Science* **226**, 829.

Hawley, M. E.: 1985, 'Comparison of Volume-Weighted Mean Concentrations in Precipitation Chemistry', *Proceedings, Ninth Conference on Probability and Statistics in the Atmospheric Sciences*, American Meteorological Society, Boston, 1985.

Keene, W. C. and Pszenny, A. A.: 1986, (pers. comm.).

Keene, W. C., Pszenny, A. A., Galloway, J. N., and Hawley, M. E.: 1986, *J. of Geophysical Research* **19**, 6647.

Liljestrand, H. M. and Morgan, J. J.: 1979, *Tellus* **31**, 421.

Miller, J. M.: 1974, 'A Statistical Evaluation of the U.S. Precipitation Chemistry Network', *Precipitation Scavenging*, ERDA Conference 741003, pp. 639–659.