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Effect of Censoring Trace-Level Water-Quality Data on Trend-Detection Capability

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■ Monte Carlo experiments were used to evaluate whether trace-level water-quality data that are routinely censored (not reported) contain valuable information for trend detection. Measurements are commonly censored if they fall below a level associated with some minimum acceptable level of reliability (detection limit). Trace-level organic data were simulated with best- and worst-case estimates of measurement uncertainty, various concentrations and degrees of linear trend, and different censoring rules. The resulting classes of data were subjected to a nonparametric statistical test for trend. For all classes of data evaluated, trends were most effectively detected in uncensored data as compared to censored data even when the data censored were highly unreliable. Thus, censoring data at any concentration level may eliminate valuable information. Whether or not valuable information for trend analysis is, in fact, eliminated by censoring of actual rather than simulated data depends on whether the analytical process is in statistical control and bias is predictable for a particular type of chemical analyses.

Introduction

Certain key types of water pollutants, principally synthetic organic compounds and some metals, often occur only in trace-level concentrations and yet are environmentally important at trace levels. Trace-level concentrations are herein defined as being so low that their detection and identification based on a single analytical determination is reasonably in doubt—the probability of incorrectly deciding that the compound is present is greater than about 5%. Both imprecision and the potential for systematic error in quantitative measurements of trace levels are generally high and poorly understood. The combination of uncertain detection and poor reliability of trace-level measurements has led laboratories to adopt rules that specify concentration levels, usually referred to as detection limits but called data-reporting limits in this report, below which measurements are not reported to data users. From the standpoint of statistical data analysis, this practice results in "censored" data sets. The term censored is used strictly in the statistical sense and is not intended to imply that laboratories are intentionally withholding valuable information or have anything but the data users' best interest in mind. Measurements that are censored are usually reported as "not detected" or as "less than" the reporting limit.

Many typical statistical analyses such as comparisons of means or variances and regression analyses are difficult or impossible to apply to censored data sets (*1*). The reliability of statistical analyses that can be applied to censored data generally decreases as the degree of censoring increases. The adverse effects of censoring are particularly acute for data on trace-level contaminants of surface waters because dilution is commonly great, resulting in low concentrations and high degrees of censoring. For example, quaterly data collected for 5 years at more than 150 stations as part of the National Pesticide Monitoring Network for Rivers indicate that more than 95% of measured concentrations for 25 pesticides were censored. Such degrees of censoring and resulting difficulties with statistical analysis may not be important for chemicals that have environmental effects only at high concentrations. But, for many of the 25 pesticides, for example, data-reporting limits were near or above water-quality criteria.

Censoring according to data reporting limits that are above concentrations that may have adverse effects on

water quality or give early indication of a trend toward such concentrations is not desirable. There are two possible approaches to alleviating this situation. First, better analytical methods may be available or might be developed that would allow lowering data reporting limits even though the limits would still be determined by the same reliability criteria. Second, the same analytical methods can be used but with lower or no reporting limits so that less reliable measurements are reported. Or, both the method could be improved and the reliability limit could be relaxed. The present study was aimed at investigating the potential benefits of lowering or eliminating data reporting limits applied to data with different degrees of measurement uncertainty.

The purpose of this report is to demonstrate that trace-level data that are routinely censored may contain valuable information despite their greater uncertainty, and that, given certain conditions, adopting a "no censoring" rule increases the data analyst's ability to detect actual trend in data. This conclusion was reached by the Monte Carlo experiment described in this report. Trace-level organic data were simulated with best- and worst-case estimates of measurement uncertainty, various degrees of linear trend, and different censoring rules. The resulting classes of data were subjected to a nonparametric statistical test for trend. The effect of different degrees of censoring is shown by comparing the power (effectiveness) of trend detection, as determined from Monte Carlo experiments, for the different classes of data with different censoring rules.

Background on Study Approach and Trend-Detection Method

While a strong argument can be made for not censoring data simply because they are the best concentration estimates available, direct demonstration of the information lost due to censoring is difficult. Systematic error may be great and is highly uncertain, and the effectiveness of parametric (distribution-dependent) analyses is difficult to ascertain. Questionable or unsupportable distributional assumptions are required to apply parametric analyses to censored data. Some nonparametric (distribution-free) statistical analyses, however, can be legitimately applied to both censored and uncensored data. A key example is a nonparametric test for trend over time, originally described by Mann (*2*) as a particular application of Kendall's τ (*3*), and which was described for application to water-quality data by Hirsch and others (*4*). Trend is here defined as a monotonic change in magnitude with time. Analysis for trend is one of the most basic and important types of water-quality assessment. Kendall's τ trend test is valid even for data that are biased, as long as the relationship between bias and concentration is constant over time. The test is not valid if changes occur over time in the relationship between concentration and bias that are not corrected for before applying the test. In general, if a change occurs in the relationship between variance and concentration, changes in the relation between bias and concentration should also be suspected.

Kendall's τ trend test provides a tool for evaluating the loss of information incurred by censoring. This evaluation is accomplished in this study by application of the trend test to both censored and uncensored versions of a large number of data sets. The trend test can be applied to censored data with no difficulty, by considering all of the censored values to be tied with each other and to be less than all noncensored values. The correction for ties (*3*) is then used in computing the variance of the test statistic.

Simulation of Data

Simulated data were used in our experiments because no trace-constituent data were available for concentrations below present-day data reporting limits and no data for higher concentrations of trace constituents or for macroconstituents had comparable degrees of measurement uncertainty. Simulated data were designed to be representative in terms of concentration levels, measurement uncertainty, and censoring levels, of data that might be observed for such trace-organic constituents as the chlorinated hydrocarbon and organophosphorus groups of pesticides. Analytical laboratories have a long history of experience with these chemicals compared to other trace-organic compounds and, thus, chemists are able to provide useful estimates of measurement uncertainty even at the very low concentrations below present data-reporting limits. The general approach taken for generating synthetic data sets was to (1) specify a probability distribution that would typically describe the population of concentration values at a river water-quality station, (2) estimate the probable worst-case and best-case estimates of measurement uncertainty, and (3) add various amounts of linear trend to the data. Representative classes of data sets were simulated by varying the underlying population parameters and the measurement uncertainty. Different censoring rules were then applied to the resulting data sets.

Population of Concentrations. Populations of concentrations occurring in samples of water taken at a river station, under the condition of no trend, were simulated to follow log–normal distributions, which describe the distribution of many water-quality data. If $y = \ln x$, where x is the actual concentration of a chemical, then the probability distribution of y is normal with a mean, μ_y, and variance, σ_y. The mean and variance of y are readily computed from the mean and variance of x (*5*):

$$\mu_y = \ln(\mu_x) - 0.5[\ln[(\sigma_x/\mu_x)^2 + 1]] \quad (1)$$

$$\sigma_y = [\ln[(\sigma_x/\mu_x)^2 + 1]]^{1/2} \quad (2)$$

For generating data sets for the Monte Carlo experiments, the population mean, μ_x, and coefficient of variation, σ_x/μ_x, were specified at desired levels and used to calculate μ_y and σ_y. Then a data set of true concentrations, x_i, of any number of values, n, could be generated by

$$x_i = \exp(\mu_y + \sigma_y \epsilon_i) \quad (3)$$

where ϵ_i is a randomly chosen value from a normal distribution with a mean of zero and variance of one.

Measurement Uncertainty. The true concentration of a trace constituent in the ith sample is x_i, but the attempt to measure x_i is imperfect and results in a measurement u_i. The value u_i is an uncertain estimate of x_i. To simulate the uncertainty associated with u_i, the probability distribution of measurements about x_i was estimated. Estimation of this distribution is difficult because, in the range of interest (at or below present detection limits), there are no actual data documenting analytical capabilities. Therefore, best-case and worst-case total-error limits estimated by two experienced chemists were used as the basis for approximating best- and worst-case error distributions.

The chemists estimated total-error limits by considering the potential for both systematic and random error (*6*). As applied in this study, the limits describe the range about a true concentration in which there is a "very high" probability that the measurement lies. For trace analyses the lower bound is always zero if negative measurements are not reported and the upper bound, or very high

Table I. Estimated Total-Error Bounds for Typical Pesticide Analyses at Various Concentration Levels (8)

concn, μg/L	best-case uncertainty estimate (measurement as percentage of true concentration)	worst-case uncertainty estimate (measurement as percentage of true concentration)
0.02	0–150 (160)[a]	0–200 (250)[a]
0.005	0–200 (190)	0–500 (400)
0.001	0–400 (350)	0–1000 (1200)
0.0005	0–500 (550)	0–2000 (2200)

[a] Values in parentheses are those computed from eq 4 and 5, which approximate the chemists' estimates.

probability level, is arbitrarily taken to represent the 98th percentile of the measurement distribution. The issue of whether or not negative values should be reported is not important to this study, but the reader is referred to ASTM (7) on this topic.

Estimated total-error bounds are shown in Table I for representative trace-level concentrations. For example, the best-case 98th percentile for 0.02 μg/L is 150%, or 0.03 μg/L, so that about 98% of the measurements of a true concentration of 0.02 μg/L would be expected to be between 0 and 0.03 μg/L. For estimation of the 98th percentile, $u_{i,98}$, of measurements of any true concentration, x_i, simple linear equations were used to approximate the best- and worst-case error bounds estimated by the chemists. Least-squares regressions were evaluated for the pairs of x_i and $u_{i,98}$ estimated by the chemists for both best- and worst-case scenarios. Slopes of the least-squares equations were adjusted within their standard error bounds to improve the fit in the low concentration range, for which most of our analysis was conducted. The equations allow rapid estimation of percentiles in the simulations. The best-case (lowest uncertainty) equation is

$$u_{i,98} = 0.002 + 1.5x_i \quad (4)$$

The slope was changed to 1.5 from the least-squares value of 1.4 ± 0.1. The worst-case (greatest uncertainty) is

$$u_{i,98} = 0.010 + 2x_i \quad (5)$$

where $u_{i,98}$ is in micrograms per liter. The slope for eq 5 was changed to 2.0 from the least-squares value of 1.5 ± 0.6. Estimates of $u_{i,98}$ from eq 4 and 5 are given in percent $[(u_{i,98} \times 100)/x_i]$ in Table I for the concentrations shown and are shown as a function of concentration in Figure 1.

Given a generated true concentration, x_i, we derived the measurement error distribution from the estimate of the 98th percentile. The error bounds in Table I suggest a measurement error distribution with positive skew. The distribution of measurements, u_i, was therefore assumed to be log normal, such that w_i is normal where $w_i = \ln u_i$, because there is greater room for error in the positive direction from the actual value. Note that the choice of a log normal distribution means that no simulated measurements will be equal to zero, when in reality some measurements may be zero or even negative. Further, the median of the distribution of measurements was assumed to equal the true concentration because the chemists felt that, even given the lopsided potential magnitude of errors in the positive and negative directions, overestimates and underestimates would occur at about the same frequency. Therefore, by the properties of the logarithmic transform

$$\mu_{w_i} = \ln (x_i) \quad (6)$$

$$w_{i,98} = \ln (u_{i,98}) \quad (7)$$

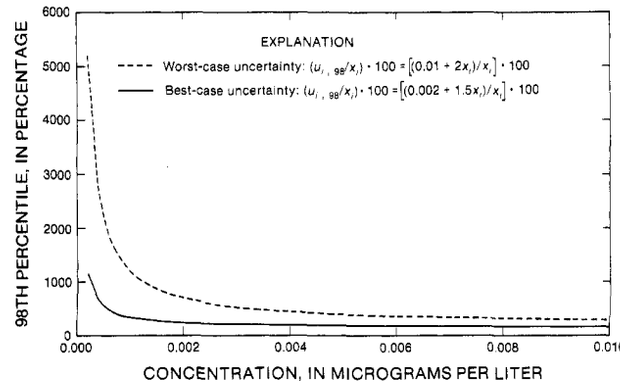

Figure 1. Ninety-eighth percentile of measurement distribution, $u_{i,98}$, as a function of the true concentration, x_i.

By the properties of the normal distribution, the standard deviation of measurements in log space can be computed:

$$\sigma_{w_i} = (w_{i,98} - \mu_{w_i})/2.055 \quad (8)$$

Values of the transformed variable, w, can then be generated by

$$w_i = \ln (x_i) + \sigma_{w_i}\epsilon_i \quad (9)$$

where ϵ_i is normally distributed with a mean of zero and variance of one. Finally, the simulated data in actual concentration units, with measurement uncertainty incorporated, are

$$u_i = \exp(w_i) \quad (10)$$

Addition of Trend. The foregoing relationships allow the generation of realistic trend-free sets of trace-constituent data. Linear trend is simple to add by causing the specified population mean, μ_x, to increase at a constant rate, m, with time, t. The coefficient of variation was left constant at the original value, σ_x/μ_x, implying that the standard deviation, σ_x, increases with μ_y. Thus, the data-generating procedure is altered at eq 1 as follows:

$$\mu_y = \ln (\mu_x + mt) - 0.5[\ln [(\sigma_x/\mu_x)^2 + 1]] \quad (11)$$

The standard deviation in log space, σ_y, is constant over time (eq 2). For the Monte Carlo experiments, 10 different positive trends (m) were added to each data set generated. The amount of trend added increased from the no-trend case to the maximum trend in equal increments. The maximum trend was determined by trial and error to best facilitate comparison of Monte Carlo results.

Summary of Data-Generating Algorithm. Data sets of any length are generated by the following steps: (1) A log normally distributed set of true water-sample concentrations, x_i, with any specified initial mean, μ_x, coefficient of variation, σ_x/μ_x, and trend slope, m, is generated by eq 11 and 3. (2) Given x_i from step 1, best- and worst-case estimates of log measurement standard deviation, σ_{w_i}, are computed by eq 4–8. (3) Given x_i and σ_{w_i}, individual measurements, u_i, are generated by eq 9 and 10.

Characteristics of Simulated Data. Simulated data sets and censoring rules were designed to be as realistic as possible. All uncensored data sets contain 40 simulated measurements. This represents, for example, 10 years of data from the National Pesticide Monitoring Network for Rivers, operated by the U.S. Environmental Protection Agency and the U.S. Geological Survey, for which sampling was quarterly. Four classes of data, where data in a class are from the same population at time zero and have the same measurement uncertainty, were evaluated in the Monte Carlo experiment.

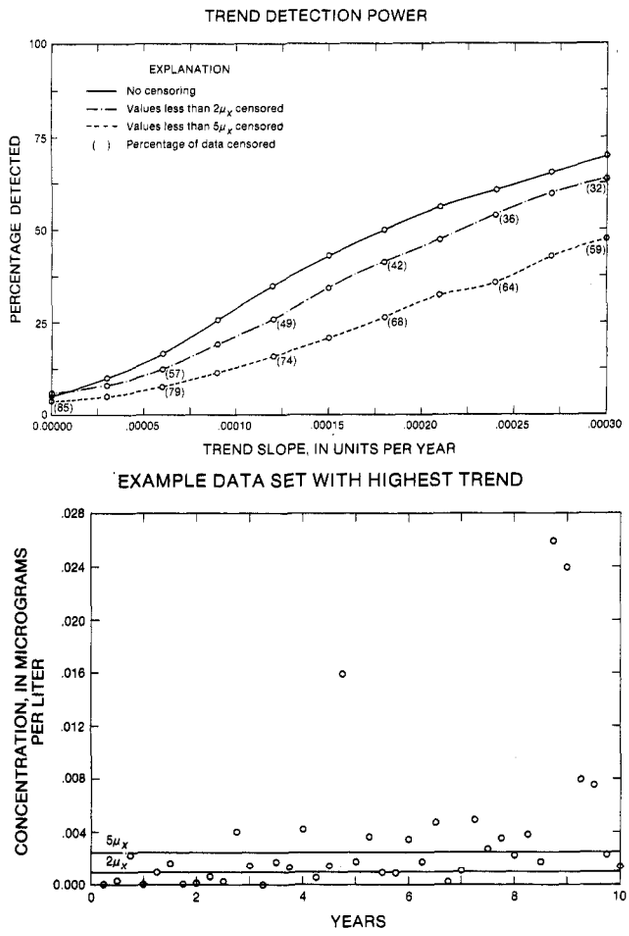

Figure 2. (Case 1) Effect of censoring on trend-detection power for data with lowest population mean, μ_x = 0.0005 μg/L, and highest measurement uncertainty, eq 5.

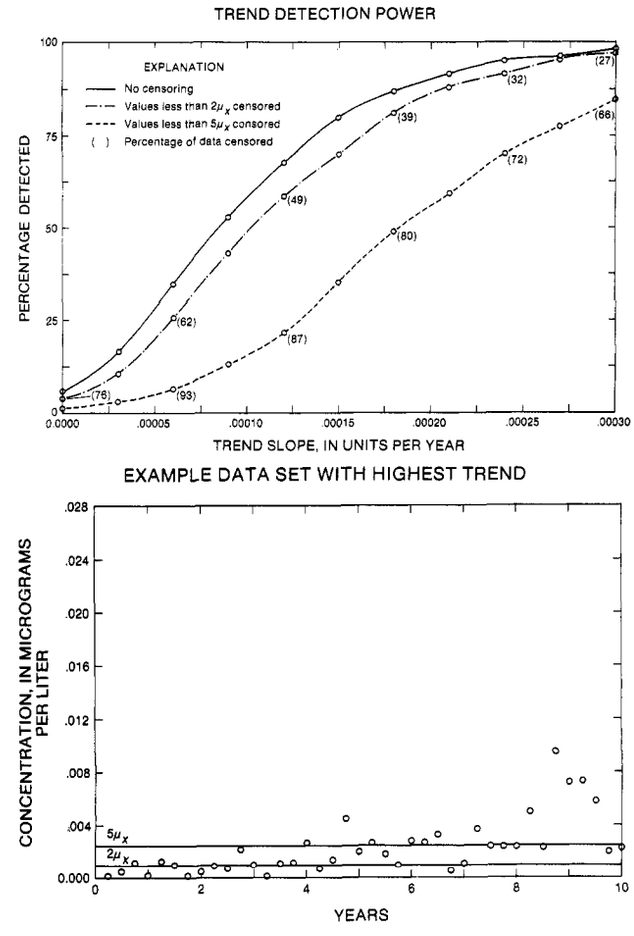

Figure 3. (Case 2) Effect of censoring on trend-detection power for data with lowest population mean, μ_x = 0.0005 μg/L, and lowest measurement uncertainty, eq 4.

Class 1: Low Population Mean and High Measurement Uncertainty. The trend-free population mean of 0.0005 μg/L was chosen to be well below routinely applied censoring levels applied to most trace-organic data, which typically range from 0.001 to 0.05 μg/L. As for all classes of data, the coefficient of variation of the population was specified to be 0.5. The measurement uncertainty specified was the worst-case relationship shown in Figure 1 and described in concentration terms by eq 5. In the absence of trend, most data in this class are censored by most laboratories, and the uncertainty in an individual measurement is extremely high.

Class 2: Low Population Mean and Low Measurement Uncertainty. This class is identical with the first except that best-case estimates of measurement uncertainty were used. These uncertainty estimates are shown in Table I and are expressed by eq 4. In the absence of trend, most data in this class would normally be censored, but the simulated measurement uncertainty is not as great as in class 1.

Class 3: High Population Mean and High Measurement Uncertainty. The trend-free population mean of 0.005 μg/L was chosen to be at a level where, given the population variability (coefficient of variation = 0.5) and measurement error, a substantial number of measurements would be above the censoring level of some laboratories (in the absence of trend). The measurement uncertainty was determined from the worst-case relationship, eq 5. Data in class 3 have smaller percent standard errors than data in either class 1 or class 2.

Class 4: High Population Mean and Low Measurement Uncertainty. Class 4 data are identical in character to class 3 data except that measurement uncertainty is lower as described by eq 4. As shown in Figure 1, however, the difference in measurement reliability between the best and worst cases is not as large at this concentration level compared to the lower levels.

Censoring Rules. Three censoring rules were applied to each generated data set, regardless of the class, resulting in three sets of data for trend analysis from each iteration of the data-generation procedure. The three censoring rules were (1) no censoring, (2) all values less than $2\mu_x$ were censored, and (3) all values less than $5\mu_x$ were censored. Recall that μ_x is the initial mean concentration. These rules were chosen to yield a representative range of presently used censoring rules. The application of the second and third censoring rules to the four classes of data yields a representative range of data that would be available to data users under present-day censoring practices and the expected range of measurement errors. A common condition not considered, but easily inferred from the tests conducted, is even more severe censoring.

Monte Carlo Experiments

The Monte Carlo experiments consisted of generating 500 data sets of a particular class and applying the nonparametric test for trend, Kendall's τ at α = 0.05, to each data set at a range of trends (10 values of m starting with

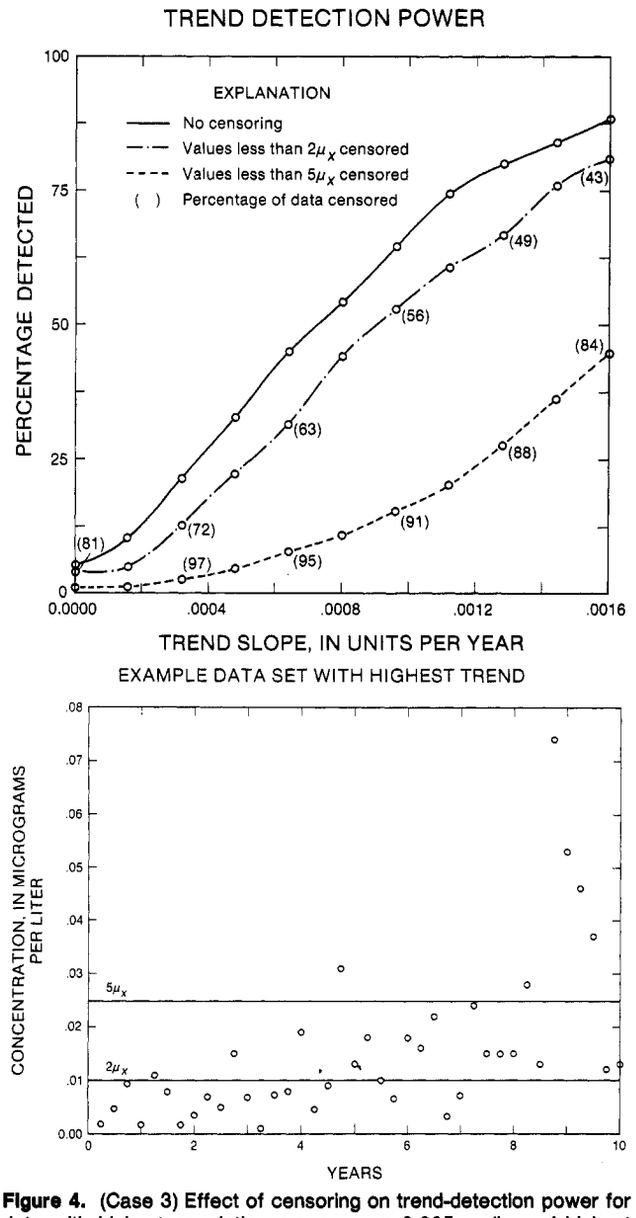

Figure 4. (Case 3) Effect of censoring on trend-detection power for data with highest population mean, μ_x = 0.005 μg/L, and highest measurement uncertainty, eq 5.

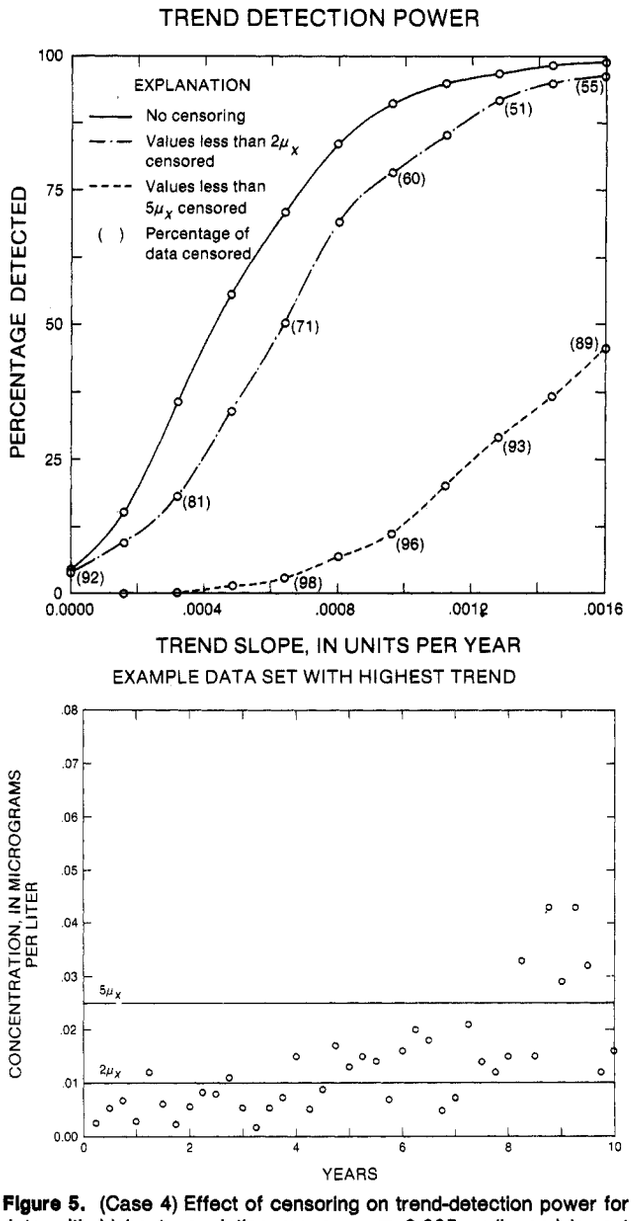

Figure 5. (Case 4) Effect of censoring on trend-detection power for data with highest population mean, μ_x = 0.005 μg/L, and lowest measurement uncertainty, eq 4.

m = 0) for each of the three censoring levels. The results of these experiments can be expressed by showing the frequency that trend was detected in the 500 iterations as a function of degree of trend for each censoring rule. This amounts to expressing the relationship between power (effectiveness) of trend detection and degree of censoring.

Results of the Monte Carlo experiments are shown in Figures 2–5. Each figure shows trend-detection power related to trend slope for each of the censoring levels. Also shown in each figure is an example data set from simulations for that data class at the maximum trend level. The actual trend units are not important because they are difficult to interpret and the reader is referred to the graphs of the data for a visual indication of the degrees of trends added. A progressively increasing level of data reliability occurs from Figure 2 to Figure 5. However, there is a much greater difference between best-case (Figure 2) and worst-case (Figure 3) estimates of uncertainty for the low concentration data classes than for the highest concentration classes (Figures 4 and 5). This reflects the greater uncertainty about the reliability of data at very low concentrations.

Results in Figures 2–5 show that, for all conditions evaluated, (1) detection of actual trend was more reliable for uncensored data compared to censored data and (2) the detrimental effects of censoring increase with increasing reliability of data. That detection of actual trend is more reliable for uncensored data is demonstrated by the solid curves representing trend detection for uncensored data in Figures 2–5, which are always above the trend-detection effectiveness for censored data. The increasing detrimental effects of censoring as data reliability increases is shown by comparison of results for class 1 data in Figure 2 and class 2 data in Figure 3, between which the only difference is measurement uncertainty. Comparison of results for class 3 data in Figure 4 and class 4 data in Figure 5 shows the same phenomenon. For both sets of comparisons the difference between trend-detection efficiency for uncensored data compared to that for the most censored data is greater for the lowest measurement uncertainty. Adverse effects of censoring increase with increasing data reliability because more reliable data contain more information than less reliable data and, thus, more information is lost when data are censored.

Discussion and Conclusions

For all classes of data evaluated, trends were most effectively detected in uncensored data as compared to censored data even when the data censored were highly unreliable. Censoring data at any concentration level, especially given our lack of knowledge about prevailing concentrations, may eliminate valuable information. The more reliable the data censored, the greater the information lost and the more detrimental the effects of censoring.

Whether or not valuable information for trend analysis is in fact eliminated by censoring of actual rather than simulated data depends mainly on whether bias is predictable for a particular type of chemical analyses and the measurement process is in statistical control. To be in statistical control, the location and shape of the measurement error distribution must be reasonably constant at each concentration. If there are changes in bias over time that are unknown and cannot be compensated for, then valid trend tests are not possible.

The use of simulated data in this study assured statistical control and a constant and predictable relation between bias and concentration. How well and how commonly this condition would be met for actual trace-level measurements is presently difficult to assess except on a case-by-case basis. In general, the condition probably holds true for measurements made by one laboratory by a constant measurement process. If the measurement process changes over time, or if measurements from more than one laboratory are to be used, then the required condition of a constant relation between bias and concentration may well not be met. In either of these cases, only careful evaluation of and correction for differences in bias would allow valid use of the data for trend analysis. Note that the need for such evaluations applies equally to data that are above present data reporting limits—these reporting limits are not magic boundaries for the absence or presence of statistical control.

The results of the present study lend strong support to the argument, earlier advanced by Rhodes (*1*) and generally followed in new ASTM standards (*7*), that data should not be routinely censored by laboratories. Uncensored data should always be retained in permanent records available to data users even if policy makers of a laboratory decide that some censoring or other form of qualification is necessary before general public release of data. Measurement data should not be discarded unless the lack of statistical control in the measurement process is clearly demonstrated.

Registry No. Water, 7732-18-5.

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Determination of Subnanogram per Liter Levels of Earthy–Musty Odorants in Water by the Salted Closed-Loop Stripping Method

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■ Grob closed-loop stripping analysis (CLSA), coupled with gas chromatography/mass spectrometry (GC/MS), has been used to analyze for low levels of earthy–musty odorants in potable water supply systems. An increase in both sensitivity and stripping rate has been achieved by raising the ionic strength of the water samples with sodium sulfate (Na_2SO_4) before stripping. Concentrations from 0 to 300 g/L Na_2SO_4 were studied. A practical condition of 80 g/L Na_2SO_4 was combined with a shorter 1.5-h stripping time to double the sensitivity of the unsalted 2-h CLSA. A detection limit of 0.8 ng/L was achieved for each of the following earthy–musty compounds: 2-isopropyl-3-methoxypyrazine, 2-isobutyl-3-methoxypyrazine, 2-methylisoborneol, geosmin, and 2,3,6-trichloroanisole. The method was validated by comparison, precision, and accuracy studies using natural source-water samples. Recoveries of dosed geosmin and 2-methylisoborneol were 105 ± 15% and 106 ± 15%, respectively. This salted procedure is a valuable modification of the CLSA when higher sensitivity or reduced stripping time is required.

Introduction

Water utilities have long been plagued by recurring earthy–musty taste and odor problems. Two such odorants, geosmin and 2-methylisoborneol (MIB), have been implicated in incidents throughout the world (*1–3*). They are secondary metabolites of certain blue-green algae and actinomycetes (*4–7*). These odorants, which have been found periodically in source-water reservoirs of The Metropolitan Water District of Southern California (Metropolitan) during the past 4 years, were the primary target of this study. Detection of concentrations below the odor threshold can act as an early warning procedure, permitting utilities to take action to avoid or mitigate an odor problem. Three other earthy–musty compounds, 2-isopropyl-3-methoxypyrazine (IPMP), 2-isobutyl-3-methoxypyrazine (IBMP), and 2,3,6-trichloroanisole (TCA), were also studied.

These five earthy–musty odorants have odor thresholds at low nanogram per liter levels (*8–12*) which are well below the detection limits of classical analytical techniques. Two methods developed for concentrating trace organics in water are the purge-and-trap technique (*13*) and closed-loop stripping analysis (CLSA) (*14*, *15*). The purge-and-trap technique has been used to detect relatively insoluble, volatile organic compounds at low microgram per liter levels. In 1980, the Master Analytical Scheme (*16*) presented a "salted-out" modification of the purge-and-trap

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