July 19, 1995

EPA-SAB-DWC-95-015

Honorable Carol M. Browner
Administrator
U.S. Environmental Protection Agency
401 M Street, SW
Washington, DC 20460

Subject: Science Advisory Board (SAB) Review of Issues Related to the
             Regulation of Arsenic in Drinking Water

Dear Ms. Browner:

The Office of Water (OW) is developing the technical foundation for the regulation of arsenic in drinking water. On August 18-19, 1994, the Drinking Water Committee (DWC) of the Science Advisory Board (SAB) reviewed several issues of concern relative to the development of this regulation. Specifically, the Committee reviewed Agency activities regarding: a) the methods being considered by the Agency to estimate national occurrence levels of arsenic in drinking water; b) the Agency's approach to determining Best Available Technology (BAT) for arsenic removal from drinking water; c) the basis for selection of quantitation detection limits for arsenic; and d) the Agency's approach to the development of a "decision tree" for a regulatory impact assessment for arsenic in drinking water.

Although the estimation of the health effects from exposure to arsenic were not the subject of this review, the Committee wishes to reiterate its concern that the available data do not allow the estimation of the magnitude of risks associated with environmental exposures to arsenic, and that a research strategy to resolve these issues is necessary. We would like to call to your attention earlier reports that addressed this issue (SAB, 1989, 1992, 1994).

With regard to the analytical issues, the Committee recommended that the Practical Quantitation Limit (PQL) for arsenic be set using acceptance limits that are similar to those used for other inorganic substances with currently approved analytical methods. It was also the Committee's opinion that risk management issues should not

enter into the procedure for determining the allowable error for the PQL. Lastly, if the PQL set using the acceptance limits described above does not meet EPA's needs, the Agency should consider and develop alternative analytical methods.

With regard to the use of censored survey data to estimate the occurrence of arsenic in drinking water, the Committee questioned the suitability of older data sources, such as those from the National Inorganics and Radionuclides Survey, and recommended that they be abandoned if sufficient new data become available. To use existing data, the Committee recommended the use of certain statistical methods that are described in some detail in the attached report.

This report also addresses a number of issues concerning Best Available Technology for arsenic removal from drinking water, including the use of ozone as a pre-oxidant for arsenic, counter-current flow ion exchange processes, reverse osmosis, and nanofiltration. However, the Committee felt that although the problems with nanofiltration technology should be solvable, the technology needs to be developed further if this is to be considered BAT for arsenic.

Finally, the Committee supported the concept of a decision tree to guide the process of determining the best approach to provide drinking water with acceptable levels of arsenic. They recommended, however, that the decision tree be expanded to incorporate a more holistic "optimization" approach, that is; one that seeks to jointly minimize the levels of all toxic chemicals and microbial agents.

We look forward to your response to the recommendations in the attached report and to further examination of the difficult technical issues underlying the regulation of arsenic in drinking water.

Sincerely,

Dr. Genevieve M. Matanoski, Chair
Executive Committee
Science Advisory Board

Dr. Verne A. Ray, Chair
Drinking Water Committee
Science Advisory Board

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ABSTRACT

The Drinking Water Committee of the Science Advisory Board (SAB) met on August 18-19, 1994 to review several issues relevant to the Agency's regulation of arsenic in drinking water; namely analytical methods, best available technology, national occurrence, and the development of a "decision tree" for a regulatory impact assessment for arsenic in drinking water.

In its report, the Committee highlights earlier SAB reports regarding the health effects of arsenic, and makes recommendations regarding the adoption of practical quantitation limits (PQL) for arsenic, the exclusion of risk management issues from the procedures for determining the allowable error for the PQL, and for dealing with PQL error ranges. In addition, the Committee questioned the suitability of older data sources for estimating the occurrence of arsenic, and recommended the use of certain statistical methods that are described to derive such estimates from existing data.

The Committee also addressed a number of issues concerning Best Available Technology (BAT) for arsenic, including the use of ozone as a pre-oxidant for arsenic, counter-current flow ion exchange processes, reverse osmosis, and nanofiltration.

Finally, the Committee supported the concept of a decision tree to guide the process of determining the best approach to provide drinking water with safe levels of arsenic, with some reservations.

Key Words: Arsenic; As; Best Available Technology; BAT; PQL; water quality

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Arsenic Review Panel

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1. EXECUTIVE SUMMARY

The Drinking Water Committee of the Science Advisory Board (SAB) met on August 18-19, 1994 to review several issues of concern relative to the regulation for arsenic in drinking water, namely analytical methods, best available technology, and occurrence. The Committee report also highlights earlier SAB reports regarding the health effects of arsenic.

With regard to the analytical issues, the Committee recommended that the PQL be set using acceptance limits for approved analytical methods that are similar to those used for other inorganic substances, rather than the ±40 percent that is now being proposed. It was also the Committee's opinion that risk management issues should not enter into the procedure for determining the allowable error for the PQL. Lastly, if the PQL set using the acceptance limits described above does not meet EPA's needs, the Agency should develop alternative analytical methods.

With the regard to questions of Best Available Technology (BAT), the Committee felt that pre-oxidation of arsenic with ozone is expected to perform well, although some issues remain to be investigated. They did not consider that oxidation would be necessary for most surface waters, but recommended that periodic analysis of speciation be required to demonstrate that oxidation is not required. The Committee urged that careful consideration must be given to the formation of disinfection by-products (DBPs) in any specification that pre-oxidation be part of BAT. They found that if ion exchange is to be used, the most appropriate choice of systems will probably be the single, deep bed, counter-current flow ion exchange process, but they questioned whether ion exchange would be an appropriate process selection for small systems. Also, they felt that corrosivity of ion exchange product water could be a problem, and that developmental research would be needed to determine how best to control the problem.

The Committee concluded that EPA should ensure that appropriate studies are conducted to determine which processes are BAT. In the Committees' view, it should be possible to conduct generic studies, as opposed to site specific studies, on reverse osmosis (RO) and nanofiltration (NF) as BAT. They found that water rejection and brine disposal would be important issues in most regions, water-scarce or not. It was not apparent to the Committee that greensand filters will be effective for arsenic oxidation, and they recommended that performance data be obtained to show the effectiveness of this approach before it is included as part of BAT. Also, the Committee

felt that although the problems with nanofiltration technology should be solvable, the technology needs to be further developed if this is to be considered the BAT for arsenic. In addition, the Committee questioned the suitability of older data sources and recommended the use of certain statistical methods that are described to derive estimates from existing data with multiple detection limits.

2. INTRODUCTION

2.1 Background

The Office of Water is developing the technical foundation for the regulation of arsenic in drinking water. On April 18-19, 1994, the Drinking Water Committee (DWC) of the Science Advisory Board (SAB) held a public meeting to review several issues of concern relative to the development of this regulation. The Committee had previously offered advice concerning the Agency's activities regarding arsenic in drinking water. Although the health effects of arsenic were not the subject of this review, section three of this report summarizes the highlights of the Committee's earlier views regarding this issue (SAB, 1992). The subsequent sections contain the Committee's responses to the specific questions in the charge in each of the four areas listed below.

2.2 Charge to the Committee

The Committee reviewed Agency activities regarding:

a)   the methods being considered by the Agency to estimate national occurrence levels of arsenic in drinking water;

b)   the Agency's approach to determining Best Available Technology (BAT) for arsenic removal from drinking water;

c)   the basis for selection of quantitation detection limits for arsenic; and

d)   the Agency's approach to the development of a "decision tree" for a regulatory impact assessment for arsenic in drinking water.

3. HEALTH EFFECTS

The health hazards associated with environmental and occupational exposure to arsenic have been the subject of several reviews by the Science Advisory Board (SAB, 1989, 1992, 1994). In these reviews, little question has been raised over the issue of whether arsenic is a human carcinogen. However, the DWC has repeatedly raised concerns on the adequacy of available data for purposes of estimating the magnitude of risks associated with environmental exposures to arsenic. It is not our intent to reiterate our technical concerns in detail here, but would like to call your attention to one review (SAB, 1992) in which considerable effort was exerted by the DWC to identify a research strategy that would help resolve these issues. The Committee understands that some of this work has been initiated by the Health Effects Research Laboratory, but most of the more substantive issues identified in the Committee's earlier report remain unaddressed.

The DWC believes that a research program directed at resolving the quantitative risk assessment issues with arsenic can be accomplished. The Committee is concerned that the Agency, in responding to short-term deadlines, will never develop the information required to make sound decisions based on science.

The relative source contribution should be clearly described in the risk characterization developed for arsenic in drinking water. The Maximum Contaminant Level (MCL) for arsenic should be set at a level that reflects understanding of the levels of arsenic contributed by other sources.

4. PRACTICAL QUANTITATION LEVELS (PQL) ISSUES

4.1 Recommendation #1

The Agency is proposing a PQL of 2 µg/L for arsenic, with acceptance limits of ±40 percent. The Committee recommends that the PQL be set using acceptance limits for approved analytical methods that are similar to those used for other inorganic substances, rather than the ±40 percent that is now being proposed.

The PQL is defined by the Agency as the "lowest level of an analyte that can be reliably measured within specified limits of precision and accuracy during routine laboratory operations" [50 FR 46906 (November 13, 1985)]. EPA further stated that the PQL is "analogous to the Limit of Quantitation (LOQ) as defined by the American Chemical Society," pointing out that the PQL is an inter-laboratory concept while the LOQ is specific to an individual laboratory [52 FR 25699 (July 8, 1987)]. The Committee agrees that a Maximum Contaminant Limit (MCL) must be set at a level that is practical for quantitation with the specified analytical method. If the MCL is not well based, the public and regulatory agencies will receive erroneous information about the safety of their drinking water.

The arsenic analytical methods that EPA proposes are not new and have been in wide use for some time. Except for the hydride method, the methods are also relatively straightforward using direct injection without derivatization or extraction steps. These conditions would suggest that a relatively low error from the true value would be chosen. For example, the analytical methods for selenium are identical to those proposed for the analysis of arsenic. The acceptance limits EPA used in establishing the selenium PQL is ±20%. In fact, the analytical procedures for all the other regulated metals are similar, and the PQL the EPA has accepted for these elements range from ±20% to ±30%. There does not appear to be any reason arsenic should be treated differently.

The Committee also notes that a plot of the percentages of laboratories passing versus the concentration of arsenic reveals that the arsenic method begins to deteriorate rapidly below a level of 4 to 6 µg/L. However, the Agency presented information that an independent PQL study supported the choice of a 4 µg/L PQL.

The Committee has observed that the Agency on occasion has introduced risk management policies into the determination of the PQL. For example, in setting the PQL for vinyl chloride, EPA stated,

> "Because of latter factor (vinyl chloride's higher potency than the other VOCs), EPA believes it is appropriate to accept slightly less precise data in order to seek to obtain more stringent levels of control [52 FR 25699 (July 12, 1987)]".

This principle has been employed several times since then. In the discussion on dioxin, EPA stated,

> "For 2,3,7,8-TCDD, EPA proposes to set the PQL at five times the Method Detection Limit (MDL). Lower contaminant levels are associated with greater difficulty in measurement and consequently less precision and accuracy. However, EPA believes it is appropriate to accept less precision if the risk posed by a carcinogenic contaminant at a level of ten times the MDL is greater than the 1×10^{-4} maximum individual lifetime risk that is generally considered by the Agency to be acceptable [52 FR 30416 (July 25, 1990)]."

Because the concentration of 2 µg/L corresponds to the Agency's current estimate of the 10^{-4} risk level, it appears that the Agency is again using risk considerations to establish the PQL. It is the Committee's opinion that the PQL would be a stronger scientific concept if risk management issues were not allowed to enter into the procedure for determining the allowable error for the PQL. The PQL for a particular analytical method should be determined based on the procedure stated in EPA's definition, namely the "lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operations."

It is the Committee's opinion that the EPA's statement that it will, "accept slightly less precise data to seek to obtain more stringent levels of control", does not accurately portray the choice being made. Lowering the hurdle for acceptable precision for an analytical method does not make it more sensitive nor does it enable the Agency to provide more stringent control. The overall accuracy and precision would not be expected to improve as a result of a lowered PQL level. Method performance will be the same as currently exists. The primary result of a lower PQL will be information of poorer quality.

The Committee agrees that different errors should be acceptable under some circumstances, but the Committee recommends that the Agency clarify its policy as to when an error of a given magnitude is acceptable. Moreover, the Committee recommends that EPA not consider the proximity to the target risk range in determining the error allowable in the PQL determination. Rather, EPA should either find or develop more sensitive methods (see discussion on analytical methods below) when the PQL which is determined does not provide satisfactory proximity.

The following principles are offered as guidance for EPA in deliberating on its analytical policy: a) greater error is acceptable when a method is new, when a method is complex, or when a method has been rarely used; and b) similar errors should be allowed when the same procedure is used to determine a different analyte unless special interferences occur. In the case of a new method, the error can be expected to diminish as it comes into more common use, so greater errors are acceptable in early Performance Evaluation (PE) data. Greater errors are also acceptable when a method involves a number of steps, like extraction or derivatization, as these additional steps inherently increase the variability of the result. Like new methods, methods that are rarely used are also likely to produce greater variability in a PE survey but will most likely produce diminished errors after they come into more common use.

4.2   Recommendation #2

If an error of ±20 or ±30 percent results in a PQL that EPA finds unacceptable, alternative analytical methods should be considered and developed as approved methods, and the data developed to establish PQLs for those methods.

Methods are presently available that can provide reliable data at levels down to and below 0.1 ppb. Many of these methods have been in use in the field of environmental analytical chemistry for many years, but for a number of reasons, they have not been used in most regulatory work. Many analysts have generated reliable data for ambient levels of arsenic in natural waters over the past 20 years. Because the range of interest in these studies has been in the range of 0.1 to a few ppb, most have utilized one of the several variations of hydride generation atomic absorption spectrometry (HGAAS), which provides capability to measure at these low levels.

The analytical community will have to modify existing methods or adopt other, proven methods in order to provide accurate and precise data at the lower concentration levels that are now of greater interest. HGAAS already has the potential

to achieve even lower levels, but may require more recent method developments than are specified in several of the HGAAS methods referenced by EPA (e.g., introduction of the hydride into a heated quartz cell rather than into an air-hydrogen flame). Graphite furnace atomic absorption spectrometry (GFAAS) offers the potential for improved data quality through repeated injection and drying, allowing introduction of larger sample volumes into the graphite tube prior to measurement. In practice, however, this may not work since matrix interferences will also increase. Samples with high dissolved solids may produce unacceptably high background signals when multiple injections are used. Unfortunately, matrix interferences are most severe at low arsenic concentrations. Minor modifications to inductively coupled plasma-mass spectroscopy (ICP-MS) methods are not detailed, but since this analytical tool is not in widespread use, its ability to support a 2 ppb PQL is limited. A general summary of these methods is presented in Table 1. While the Committee has no direct experience with detection levels resulting from a combination of hydride generation and ICP-MS, it seems reasonable that this method will also provide detection limits of at least 0.05 ppb.

The methods in Table 1 satisfy the requirements for feasibility, in that they are proven, sensitive, and within the ability of any competent analytical laboratory that perform analyses at trace levels. Further, several can be used with existing instrumentation with only the addition of a sample concentration step or a reliable instrumental module to introduce the sample to the detector.

Table 1. Approximate Detection Limits of Available Analytical Methods for Measurement of As in Drinking Water Matrices

Method	Approximate MDL (ppb As)
Column preconcentration/GFAAS (graphite furnace atomic absorption spectrometry)	0.05
Manual HGAAS (hydride generation atomic absorption spectrometry)	0.10
Continuous or flow-injection HGAAS (hydride generation atomic absorption spectrometry)	0.05
HGAFS (hydride generation atomic fluorescence spectroscopy)	0.05

5. BEST AVAILABLE TECHNOLOGY

This section contains responses to the questions posed by the Agency regarding Best Available Technology for arsenic removal. Also included are issues related to the topic that the Committee believes to be relevant.

5.1 Pre-oxidation

a)   If EPA receives performance data on ozone (O_3), are there other limitations on the use of ozone as a pre-oxidant for arsenic?

Limitations are probably fewer on the use of ozone as a pre-oxidant for arsenic than when O_3 is used after filtration as a primary disinfectant. Assimilable Organic Carbon (AOC) formation is ameliorated by coagulation/filtration treatment downstream, and oxidation of bromide, though still possible, is much less likely during pre-oxidation because the development of a significant ozone residual is not necessarily required. Ozone pre-oxidation before nanofiltration could present a problem if the AOC that is formed has a low molecular weight and passes through the membrane. This issue should be studied as part of the membrane research effort recommended in Section 5.3.

b)   Are there any generic conditions, other than speciation, that could be used to determine when pre-oxidation would not need to be a component of BAT?

Oxidation is probably not necessary for most surface waters; however, periodic analysis of speciation should be required to demonstrate that oxidation is not required. We do not know, for example, whether As(III) is found in lakes and reservoirs that periodically go anoxic.

c)   Is there an incompatibility of the requirement for pre-oxidation to convert As(III) to As(V) with the requirement to reduce disinfectant byproducts (DBPs)?

Chlorine is a good oxidant for As(III), but application must come early in the treatment train when disinfectant byproduct precursor concentration is high and there is a danger of producing large concentrations of DBPs. Permanganate may work better, but we do not have sufficient information on the permanganate demand for arsenic

oxidation relative to the demand exerted by other substances. Ozone may be the most satisfactory for such waters, but performance data are limited. This is an issue for surface waters that go anoxic, because As(V) may be converted to As(III) under these conditions, and for ground waters with high concentrations of organic matter. Careful consideration must be given to the formation of DBPs in any specification that pre-oxidation be part of BAT.

5.2   Ion Exchange

a)   Does SAB agree with the "merry-go-round" approach (i.e. series operation of columns) for ion exchange in order to meet low-level MCL options?

Series operation of columns can achieve the low levels required, but so can several other designs/operating methods. For example, operating columns using the "counter-current flow" principle of operation will increase the usable capacity of the ion exchange bed and also reduce the "leakage" (effluent level) of arsenic. In most common ion exchange designs, both the water to be treated and the regenerant go downflow through the resin bed. This "cocurrent" process can result in high "leakage" and high regenerant requirements because the regeneration process concentrates the contaminants on the effluent end of the ion exchange column. Compared to such operation the "merry-go-round" approach will result in more efficient use of the resin and achieve lower effluent concentrations. However, over the past twenty years or so, single-bed, counter-current processes have shown themselves to be more cost effective options. Instead of the "merry-go-round" approach, EPA will probably find a single, deep bed, counter-current flow ion exchange process the most appropriate choice when particularly high removals of arsenic are required.

b)   Does the SAB agree with the recommendation of ion exchange alone as a BAT primarily for small ground water systems?

The ion exchange process has the advantage of being easy to automate. However, we understand that the anion resins being considered for this process have a preference for sulfate over arsenate. As a result, if the process is allowed to run unattended, there is a potential that all the arsenic will be displaced from the column in a very short time period if the process is run to exhaustion. This problem could, perhaps, be overcome with proper operation. Further, the ion exchange resin would probably be used in the chloride form, and thus the process would result in large increases in chloride concentration in many situations. An increase in chlorides can greatly increase the corrosivity of the product water and red water problems, thereby

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introducing undesired secondary effects of this process. Membrane processes may be a more appropriate choice.

    c)   Is there a problem with using ion exchange, and coagulation/filtration followed by ion exchange, for large systems?

A primary issue here is the "corrosivity" of the product water, just as it is for small systems. Chlorides increase the corrosivity of iron and will lead to more problems with red water, especially when the high chloride levels are intermittently present. Modifications of the ion exchange process could be developed that would eliminate or minimize this problem, but developmental research is needed.

5.3 Membrane Treatment

    a)   Should pilot-scale studies be included as a component of the treatment train when EPA prepares costs for options where nanofiltration (NF) is selected to remove arsenic?

EPA should see that appropriate studies are conducted to determine which processes are BAT. It should be possible to do generic studies, as opposed to site specific studies, on reverse osmosis (RO) and NF that show whether they are BAT. NF is just a variation of RO wherein a looser, alternative membrane is used along with lower operating pressures. If sufficient information is not available to demonstrate that NF is an appropriate BAT, EPA should not consider NF and should nominate RO as BAT. Utilities who are willing to invest in pilot studies can still install NF once they are convinced it will give satisfactory performance.

    b)   Is water rejection an issue in water-scarce regions?

Yes. Disposal of reject water is an important issue in most regions, water-scarce or not. Brine or reject water disposal is one of the principle obstacles to broader application of ion exchange, reverse osmosis, nanofiltration and electrodialysis and the constraints are getting tighter, not looser. The EPA should give serious consideration to this problem.

    c)   Pre-oxidation before membrane processes.

This is an issue that requires careful research. The EPA assumes that As(III) can be oxidized to the more easily removed As(V) using a greensand filter. The greensand filter is used effectively with permanganate to remove Fe(II) and Mn(II), and

to accomplish this, permanganate is either applied continuously to the influent to the greensand or intermittently, during backwash. When applied intermittently, the mechanism is one of forming a layer of MnO_2 on the filter media that adsorbs multivalent cations. The adsorbed ions are then held until permanganate is applied during backwash. The adsorbed material is eliminated during backwash, or oxidized to insoluble forms that remain in layers on the greensand. When permanganate is applied continuously, the same mechanism applies, except that oxides of Mn and Fe continuously build up on the greensand media until they are backwashed off. Given this mechanism of operation, it is not apparent that greensand filters will be effective for arsenic oxidation. Is co-occurrence of Fe(II) essential for performance? Does MnO_2 oxidize As(III)? The Committee recommends that performance data be obtained to show the effectiveness of this approach before it is included as part of BAT.

d)   Nanofiltration technology applied to surface waters.

The water industry has great difficulty applying membrane processes to surface water because of membrane fouling and flux decline. The problems should be solvable, but the technology needs to be further developed if this is to be considered BAT for arsenic.

5.4 Coagulation, Lime Softening, and Direct Additives

a)   Is the analysis of removal data in the coagulation and lime softening processes appropriate?

A heavy emphasis has been placed on "percent removal." The mechanism of removal is probably precipitate formation or formation of a chemical bond that is concentration dependent. It makes more sense from a chemical mechanism point-of-view to analyze the data in terms of remaining concentration. For example, the removal in lime softening may be partially dependent on adsorption onto $Mg(OH)_2$ and may not be removed if this precipitate is absent. Adsorption is also dependent on solution concentration, and process effluent concentration would likely be a function of solution chemistry; percent removal in the coagulation process would then be a function of surface chemistry.

b) Does the SAB agree that the impact of arsenic in direct additives on water systems should be minimal unless a very low standard (<1 µg/L) is selected, and does the SAB agree that the impact of arsenic in indirect additives on water systems should be minimal?

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The Committee does not have access to recent data on arsenic levels in direct additives that would be necessary to make this evaluation. The analysis conducted several years ago by the National Academy of Sciences (NAS) Committee on direct and indirect additives indicated that arsenic was generally not a problem in water treatment chemicals with an MCL of 50 µg/L, and third party certification processes are established using the guidelines of that committee's effort. A significant effort would be required to review the matter in light of a revised MCL.

6. OCCURRENCE OF ARSENIC

6.1 Background

EPA is considering a change in the MCL for arsenic and would like to use existing occurrence data on arsenic in drinking water in order to make judgments about the impact of alternative regulatory targets. The Agency is considering a range for the new MCL of 2 to 20 ug/L, but the most geographically comprehensive occurrence data are found in older surveys, particularly the National Inorganics and Radionuclides Survey (NIRS), and these surveys have a Reporting Limit (RL) of about 5 ug/L. As a result, the data are censored in the sense that quantitative measurements are reported for some samples (not censored), but the remainder are only reported as less than the RL(censored).

Analytical techniques have been improving over time and additional data are available from the states and from other special purpose surveys. Many of these surveys have RLs of 0.5 to 1 ug/L, but none is sufficiently comprehensive to serve as a basis for regulation by themselves. Additional surveys of a more comprehensive nature may soon become available. EPA would like to use all these data to produce a best estimate of the national occurrence of arsenic. The problem is not just using censored data, but using censored data from a variety of sources and a variety of geography's with multiple reporting limits. EPA suggests that an error in estimating the number of systems affected by a particular MCL within a factor of two would be acceptable. The Agency's current estimates suggest that the Nation's capital cost would be $140 millions and $6,200 millions to comply with MCLs of 20 and 5 ug/L, respectively.

Using the older survey data is attractive because of the number of systems that were tested (some 47,000 in the NIRS, for example). Arsenic is a naturally occurring element that is probably present in all the samples analyzed. On the other hand, because arsenic is generally present at low levels and these surveys have relatively high RLs, the survey results consist almost entirely of censored data (e.g., NIRS 93%, CWSS 97%, and RWS 90%). The Committee recommends EPA abandon attempts to use these older data when sufficient new data become available.

The problem EPA faces in using censored data is not a new one and there exists a substantial literature on the subject. The following discussion will address only the most important elements of the subject.

6.2   Use of censored data

6.2.1   Probability density function (PDF)

If the data were not censored, they could be used to determine the parameters of a Probability Density Function (PDF) and then that PDF could be used to predict the number of water systems that would be impacted at alternative MCL values. Data on environmental chemicals are often modeled with the Log-normal PDF because it eliminates the risk of estimating negative concentrations and because it predicts mostly low concentrations except for a long tail to the right, simulating contaminated situations. The Weibull PDF has these same properties with the additional advantage that it can be integrated analytically to produce a cumulative distribution function that enables convenient estimates of the occurrence of specific concentrations (Mackay & Paterson, 1984).

6.2.2   Non-parametric methods

Alternatively, if there were enough data, they could be put in ranked order and the percentage of the systems exceeding a specified regulatory target could be estimated without recourse to more complex statistical techniques. The best scientific approach is to conduct a new survey with reporting limits below the regulatory range targeted by the risk manager. Using the results of this survey the Agency could develop a simple ranking of the data to characterize occurrence at levels being considered for regulation. This approach would avoid the complication of choosing a PDF altogether.

On the other hand, if the EPA insists on using existing data, the Committee recommends that the Agency also consider the use of nonparametric methods (methods that do not require the assumption of a specific PDF model) to estimate the distribution for concentrations that are in the range of the data. The Kaplan-Meier or product-limit estimator (Cox and Oakes, 1984), suitably modified for left-censored data, is the nonparametric maximum likelihood estimator of the distribution function in the case of censored data. Cox and Oakes (1984) provide methods for computing limits based on product-limit estimates.

6.2.3   Goodness-of-fit

It appears that the Agency has used comparisons of the estimated averages and standard deviations as well as probability plots of the data and the Kolmogorov-

Smirnov (KS) tests to evaluate the suitability of both the PDF's and the methods of estimation. The application of the KS test described to the Committee at the August 18th meeting does not appear to be appropriate.

Qualitatively, the "fit" of censored data to any particular distribution (Normal, Lognormal, Weibull, etc.) is best accomplished by observing a plot of the data on axes of an appropriate scale, on a probability plot. The Committee is not aware of a general goodness-of-fit test that is valid for censored data. The Chi-Square goodness of fit test could be applied if the data were grouped so that all of the non-detects fall in the lowest interval. However, this restriction may not permit a reasonable grouping if there are multiple detection limits.

The Kolmogorov-Smirnov test can only be used to select objectively the choice between PDFs if all the parameters of the PDFs have been determined before-hand (i.e., not from the data). For example, the KS statistic (and the corresponding plot) could be used to determine if the crushing strengths of 35 concrete test cylinders meet a specification: and that they have an average crushing strength of 4,000 psi with a standard deviation of no more than 400 psi to a 95% level of significance. The corresponding KS statistic would be 0.21. Using this statistic, a plot could be constructed on normal probability paper showing the boundaries within which the data must lie to meet the specification.

6.2.4 Simulation studies

Perhaps a better way to evaluate the suitability of alternative PDFs (and alternative methods of estimating PDF parameters from a censored distribution) is to evaluate their effectiveness in producing accurate estimates of low level concentrations of arsenic using a simulation.

If the EPA wishes to conduct a simulation evaluation of various approaches to estimating the parameters for the model selected, we recommend that EPA simulate from a completely determined distribution so that estimated quantities can be compared to known values. The following specific approach is suggested with the lognormal distribution in mind.

Using data from a suitable study, estimate the parameters u and s of the log-normal distribution by fitting a log-normal distribution to the complete data set using the maximum likelihood estimation (MLE) or regression on ordered statistics (ROS) approach (but not the Modified Delta-Lognormal, or MDLOG). Using these parameters and a random number generator, generate by computer simulation the same number of

samples as are in the underlying data set. For example, suppose in the database, a) there are two distinct values for non-detects, 5 ug/L and 10 ug/L, b) there are 1000 samples with concentrations less than or equal to 10 (including detects and non-detects), 50 of which are non-detects with detection limits of 10 ug/L and 900 of which are non-detects with a detection limit of 5 ug/L, and c) no detects have concentrations less than 5 ug/L. First, in turn, take each simulated concentration that is ≤ 10 ug/L and, with probability 50/1000, convert it to a non-detect with detection limit of 10 ug/L. Then convert each of the remaining simulated samples with concentrations less than 5 ug/L to non-detects as well. This results in a simulated data set with a pattern of non-detects that is similar to the original data set.

Generate a large number (e.g., 1000) of such simulated data sets and apply each of the estimation methods to be compared to each. With each such simulation and each estimation method evaluated, record the probability that a sample concentration exceeds 2, 5, 10, 15, 20, 30, 40, and 50 ug/L. For each of the estimation methods, prepare graphs showing the resulting distributions of probabilities as well as true probabilities. Also estimate the mean square error and the bias of each estimator.

This simulation should provide a good indication of the relative performances of the estimators whenever the true distribution is log-normal. If EPA wishes to evaluate the properties of these estimators when the log-normal assumptions not valid, the simulation could be repeated, with the only change being that the simulated data are generated using the new PDF model, presumably one that appears to better describe the data.

6.2.5 Fitting Censored Data to PDF

During the past decade a substantial literature had developed on methods for estimating the parameters of a PDF from censored environmental data. The approaches used break down into three groups that are much like those being considered by the Agency for arsenic: a) simple substitution; b) regression on order statistics (ROS); and c) maximum likelihood estimation (MLE).

Suitability of MDLOG. The Modified Delta Log normal method (MDLOG) is but one example of the simple substitution methods. It produces a distorted distribution that is not representative of the original censored population and should not be used, but because the MDLOG estimation method is widely used in the treatment of environmental data, it deserves further discussion. This method is fundamentally different from the ROS and MLE methods. Both of the latter two methods assume that the true concentrations in all samples come from a common population that is log-

normally distributed. In particular, non-detects are assumed to come from the same distribution, albeit the low end of that distribution. The MDLOG method, however assumes that a) the detects and the non-detects come from different sample populations; and b) that the detects themselves constitute an uncensored sample from a log-normal distribution. As discussed later, this latter assumption only applies if it can reasonably be presumed that the contaminant is present in some samples and absent in others - an assumption that certainly cannot be applied in the case of a naturally-occurring element like arsenic.

Whether a sample is a detect or a non-detect is determined by the RL of the analytical method. In the case of Arsenic, there would be no reason to assume that the concentrations above and below the RL come from distinct populations. (An illogical conclusion of such an assumption is that analyzing samples with methods having different RLs would lead to different underlying concentrations.) Moreover, the detects cannot represent an uncensored sample from a log-normal distribution because, whereas a log-normal distribution includes all positive values, a non-censored sample cannot assume any value less than the smallest RL of any of the samples.

A priori, it is expected that maximum likelihood estimation approach will perform the best of the these procedures. A number of studies have been published comparing these methods and showing alternative algorithms for solving the MLE problem (Hashimoto & Trussell, 1983; Gleit, 1985; Guilliom & Helsel, 1986; El-Shaarawi 1989; Haas and Scheff, 1990; Helsel, 1990; and El-Shaarawi & Esterby, 1992). These studies have consistently found the ROS and MLE procedures superior to simple substitution methods. The practical differences between the MDLOG and the ROS and MLE estimation methods can be seen from Table 2 displaying the results of applying all three methods to the NIRS data on very small systems (cf. Exhibits 3-5, 4-1, and 4-5 in the "occurrence" document given to the Committee). Estimates from the ROS and MLE methods agree closely and predict a smooth log-normal distribution throughout the range of 2 to 50 ug/L. Results from the MDLOG methods agree reasonably well with results from the other two methods in the range where most of the non-censored samples were located (5 to 20 ug/L). However, it gives very different results in the tails. The MDLOG procedure predicts that virtually 100% of the systems have arsenic concentrations greater than 2 ug/L, because of the *ad hoc* assumption that all non-detects have actual concentrations of one half the RL (which was 5 ug/L in the NIRS database). Thus, since the predictions of the MDLOG procedure at concentrations below the RL are determined solely by this assumption, the MDLOG procedure should not be used to predict the concentrations below the RL. The MDLOG procedure also predicts only one-tenth as many systems having concentrations in excess of 50 ug/L as the other two methods. Although one cannot say with certainty that the MDLOG

prediction is in error (since 50 ug/L is beyond the range of the data), the assumption that led to the smaller tail of the MDLOG distribution is erroneous (that assumption being that the parameters determined from non-censored values represent entire population and that all samples below the RL are the same which leads to a log-normal distribution with a smaller variance than that estimated under a more appropriate assumption that the non-censored samples represent a censored sample of the distribution).

Table 2. Comparison of Estimates of Cumulative National Occurrence of Arsenic in Community Ground Water Supplies (Exhibit 4-5) Using ROS, MLE and MDLOG Models.

System Size (Population Served)	No. of Systems in U.S.	Number of Systems with Concentrations (µg/L) in Excess of:											
		0.5	1	2	3	4	5	10	15	20	30	40	50
ROS Estimates (Exhibit 4-5)													
Very Small													
25-100	16634	8467	5634	3266	2216	1629	1259	508	276	173	85	49	32
101-500	15422	7850	5223	3028	2054	1510	1167	471	256	160	79	46	30
MLE Estimates													
Very Small													
25-100	16634	8223	5449	3155	2143	1578	1222	497	272	171	85	50	32
101-500	15422	7624	5052	2926	1987	1463	1133	460	252	159	79	46	30
MDLOG Estimates													
Very Small													
25-100	16634	16634	16634	16632	1198	1159	1097	644	318	153	38	11	4
101-500	15422	15422	15422	15420	1110	1075	1017	597	295	142	36	10	3

ROS and MLE methods have also been shown to produce almost the same values for PDF parameters. The ROS procedure is more stable when non-censored data are limited, but MLE methods generally produce a more precise estimate of the mean. The Committee recommends that the Agency limit its methods of estimation of PDF parameters to variations of the ROS and MLE procedures.

6.2.6 Confidence Intervals

Standard confidence interval methods are available for the product-limit estimator (Cox and Oakes, 1984). We recommend that the profile likelihood method (Cox and Oakes (1984), page 35, procedure (a)) be used to compute confidence limits for the parameters estimated by the MLE method. The ROS method does not easily lend itself to confidence limit estimates.

7. REGULATORY IMPACT ASSESSMENT DECISION TREE

The Committee believes that the concept of a decision tree to guide the process of determining the best approach to provide drinking water with safe levels of arsenic is reasonably good. In addition to guiding the selection of the best available treatment technology, the decision tree approach will have the added benefit of revealing missing information about processes needed to make such decisions. As such, it will be helpful in identifying priorities for further research in order to fill gaps in our knowledge

7.1 Does the SAB agree with the lower removal efficiency assumption for coagulation/ filtration based on full-scale data?

Yes, given the complexity of full-scale plant operation compared to carefully designed and run bench and pilot studies, the lower removal efficiency is not surprising.

7.2 Does the SAB agree that EPA should re-evaluate this assumption if the American Water Works Association (AWWA) data on existing plants examines arsenic removal at optimum conditions?

Yes.

7.3 Does the SAB agree with this revision to the design assumptions for membrane systems? (using 75% recovery)

This issue should be investigated further. Although most systems may be designed at 75% recovery regardless of the capacity, required maintenance and downtime are reduced if higher recoveries are allowed. With some designs, recoveries can be adjusted in the field over a broad range. Considering operating requirements, lower recoveries would seem appropriate for smaller systems, particularly those operating on harder water. The question is, are these field adjustments made, or are the systems just installed and operated as the designer envisioned?

7.4 Does the SAB agree with the elements to be costed for nanofiltration (including the cost of up-front cartridge filters) when high iron and/or manganese levels are present with arsenic?

Levels of iron (Fe) and manganese (Mn) even below the secondary standards will interfere with both reverse osmosis and nanofiltration, but recognizing the nature of the data available, perhaps it is acceptable to presume special treatment on systems not meeting those standards alone. Such pretreatment should include oxidation, granular media filtration, and cartridge filtration. Oxidation alternatives deserve further examination. Where possible, chlorine is most straightforward. For low levels of Fe and Mn, and where greensand is used, regeneration of the greensand with $KMnO_4$ may be used (see above comments on the greensand process). Chlorine dioxide may be appropriate in some cases as may ozonation. Continuous permanganate feed is difficult to control and should only be considered for fairly large systems. For small systems, greensand may be appropriate, but larger systems will find it more cost-effective to employ conventional sand or anthracite media and acclimate it with a MnO_2 coating.

7.5 Does the SAB agree that sludges should be classified as non-hazardous with the current or a revised arsenic standard?

Data presented are encouraging, but an adequate explanation for the results is not available. Assuming a water with 3 mg/L suspended solids, and alum dose of 50 mg/L, and an As level of 1 mg/L, the resulting sludge would be 6% (60,000 mg/kg of dry solids).

7.6 Should alternate source development be used as an alternative even for low-level options where all potential sources may contain arsenic?

Utilities accustomed to using groundwater are generally not equipped or trained to operate treatment facilities, except for the few that already treat water high in hardness or iron and manganese. As a result they will tend to look at alternate sources with greater interest. Rarely is an entire region so uniformly high in contaminants such as arsenic that alternative well fields cannot be found.

7.7   Should regionalization continue to be included at 5% even though it is generally more expensive than the BATs? The focus on system viability in the SDWA re authorization would suggest that costs continue to be developed for this option in the RIA.

It is not clear to the SAB that regionalization is consistently higher in cost. The cost feasibility of regionalization would appear to be related to the proximity of a large regional system. Perhaps systems in urban areas should have a higher percentage than those in rural environments.

The Committee also notes that there are additional aspects that should be incorporated into this decision tree process.

First, the decision tree should be expanded to incorporate a more holistic approach. Essentially, the goal should be to select appropriate treatment processes which not only minimize exposure to arsenic but to other toxic agents, both organic (e.g., trihalomethanes) and metal species as well; other compliance requirements should be achieved (e.g., disinfection by-product rule, groundwater rule, etc.). The selection of a treatment process should use an "optimization approach" that will yield the desired safe levels for all toxic chemicals and microbial agents. From a practical point of view, a municipality attempting to achieve compliance to several rules may only have resources to address the issue once; therefore, it needs to "take its best shot."

Furthermore, an estimated economic impact analysis for implementing an optimal consolidated treatment train may reflect only a modest increment in cost if distributed across several pollutants, whereas, the economic impact of implementing a treatment process may be, in fact, highly inflated when determined on a chemical-by-chemical basis.

Second, a factor that is often considered in selecting a treatment process is the potential waste products produced. The decision tree should include their production and disposal issues.

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AN SAB REPORT: REVIEW OF ISSUES RELATED TO THE REGULATION OF ARSENIC IN DRINKING WATER

REVIEW BY THE DRINKING WATER COMMITTEE (DWC) OF THE SCIENCE ADVISORY BOARD