September 5, 1997

EPA-SAB-EEC-LTR-97-011

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

Subject: To Filter, or Not to Filter; That is the Question

Dear Ms. Browner:

In its quest to identify risks from contaminated sites that may require placing a site on the National Priority List (NPL), the U.S. Environmental Protection Agency (EPA) conducts preliminary assessment (PA) and site inspection (SI) to collect information for use in its Hazard Ranking System (HRS). The HRS utilizes releases of hazardous materials data for four pathways, including release to groundwater. Obtaining a groundwater sample for chemical analysis requires the utmost care in order to preserve the chemical and physical integrity of the sample. In particular, one must decide whether or not to use filtration in the field in order to remove solids attributable to the geological formations that may be inadvertently entrained in the sample during the course of its collection. It is generally known that filters should not be used if the water is to be analyzed for organic chemicals, because many organic chemicals adsorb to the filters, thereby lowering their concentrations in the filtrate. However, whether or not to filter groundwater samples when analyzing for metals is a much more difficult question to answer.

Background

The Special Topics Subcommittee of the SAB's Environmental Engineering Committee (EEC) met on April 29, 1997 to examine this question in the context of a review of the Office of Emergency and Remedial Response's (OERR) proposed guidance on field filtration of groundwater samples taken from monitoring wells for metals analysis as a part of Superfund site assessment. The Subcommittee was charged to:

a) Provide a technical review of the proposed guidance;
b) Evaluate consistency with other Agency programs; and
c) Provide comments on the appropriateness and potential impact of the document.

The Subcommittee has developed a set of review comments focused on the technical aspects of the guidance manual. The Subcommittee s four key points are: proper well construction is important; filtration is not recommended under low flow conditions; samples should be filtered when the nephelometric turbidity units (NTU) exceeds 5 NTU; and there should be consistency on the issue across EPA.

The Agency could, as a matter of policy, decide against field filtering of groundwater samples collected for Superfund PA and SI, but it needs to be aware of the inherent technical limitations and uncertainties associated with such a decision. Note that this issue of filtration of groundwater samples from Superfund sites is separate from the issue of filtration of surface water samples from Superfund sites. The latter is a practice that is endorsed and elaborated upon by the SAB's Ecological Processes and Effects Committee in a separate report.

Key Findings and Recommendations

a) The Subcommittee finds that several factors could introduce errors in the sampling and analysis of groundwater for metals. Well construction, development, sampling, and field filtering are among the steps that could influence the metals measured in the groundwater samples. Field filtering is often a smaller source of variability and bias compared to these other factors.

   Therefore, the Subcommittee recommends that the Agency emphasize in its guidance document the importance of proper well construction, development, purging, and water pumping rates so that the field filtering decisions can also be accurately made.

b) The Subcommittee notes that under ideal conditions, field filtered groundwater samples should yield identical metals concentrations when compared to unfiltered samples. However, under non-ideal conditions, the sampling process may introduce geological materials into the sample and would require field filtration. Under such conditions, filtering to remove the geological artifacts has the potential of removing colloids (small particles that may have migrated as suspended materials that are mobile in the aquifer). Available scientific evidence indicates that field filtering should not be necessary when: (1) wells have been properly constructed, developed, purged; (2) when the sample has been collected without stirring or agitating the aquifer materials; (3) and turbidity is less than 5 NTU.

   Therefore, the Subcommittee agrees with OERR that for Superfund Site Assessments the low-flow sampling technique without filtration is the preferred sampling approach for subsequent metal analysis when well construction, well maintenance and hydro geological conditions such as

flow rate allow. Under such conditions, the collected samples should be representative of the dissolved and particulate metals that are mobile in groundwater systems. The Agency s proposal to rely on low flow sampling and unfiltered samples is a conservative approach that favors false positives over false negatives.

c) The Subcommittee is aware that when the turbidity of the sample is high, the situation is different. It also notes that in-line filtering provides samples which retain their chemical integrity.

Therefore, based on the available scientific knowledge, the Subcommittee recommends that field filtering of properly collected groundwater samples be done when turbidity in the samples is higher than 5 NTU, even after slow pumping has been utilized to obtain the sample.

d) The Subcommittee finds that there are a number of inconsistencies--real or apparent--that exist among Agency guidance documents dealing with the issue of filtering; cf., OERR, Resource Conservation and Recovery Act (RCRA), and Office of Water (OW) documents.

Therefore, the Subcommittee recommends that the Agency carefully review its technical guidance documents on filtering to make certain that they are consistent and that the differences (e.g., application to groundwater vs. surface water sampling) are identified and justified.

e) With regard to the impact, the Subcommittee finds that if samples are not filtered when they should be, then overestimation of the metals concentrations could lead to the listing of a site on the NPL, resulting in a misallocation of scarce resources while also presenting a major burden for the potentially responsible parties. On the other hand, if samples are filtered when they should not be, then the underestimation of the metals concentrations could incorrectly result in a significant site not being listed on the NPL.

Therefore, the Subcommittee observes that the Agency s proposal to rely on low flow sampling and unfiltered samples for metals analysis is a conservative approach that favors false positives over false negatives.

The Subcommittee went beyond its charge and developed the following thoughts regarding groundwater sampling when non-aqueous phase liquids (NAPLs) are present.

f) The Subcommittee finds that potential Superfund sites often have light or dense non-aqueous phase liquids (LNAPLs or DNAPLs, respectively) present in their groundwater environment. The presence of these liquids raises some important questions regarding sampling of groundwater.

Therefore, the Subcommittee recommends that the Agency address this issue in its revised guidance and that it conduct research to determine whether the low flow sampling method is appropriate when LNAPLs or DNAPLs are present.

The Subcommittee's detailed suggestions are included in the attached Appendix. We appreciate the opportunity to review and provide comments on the draft guidance and look forward to its completion by the Agency. While we address this report to you, we look forward to a written response from the Assistant Administrator for the Office of Solid Waste and Emergency Response (OSWER).

Sincerely,

Genevieve M. Matanoski

Dr. Genevieve M. Matanoski
Chair, SAB Executive Committee

Dr. Ishwar P. Murarka, Chair
Special Topics Subcommittee and
Environmental Engineering Committee

APPENDIX A

Technical elaboration on points made in the EEC Report on
"To Filter, or Not to Filter; That is the Question""
An Evaluation of Superfund Proposed National Guidance on
Collection of Groundwater Samples for Metals Analysis

1. Introduction

On April 29, 1997 the Special Topics Subcommittee of the Science Advisory Board s Environmental Engineering Committee (EEC) reviewed the Office of Emergency and Remedial Response's (OERR's) proposed national guidance on field filtration of groundwater samples taken for metals analysis from monitoring wells during Superfund site assessment USEPA, 1996). Within the scope of the Superfund Hazard Ranking System (HRS), the proposed national guidance is intended to address the question of appropriate techniques for well water sample collection and the potential influence of filtration on metals analysis. The results of these analyses are ultimately used as part of the ranking exercise to determine whether or not a given site is listed on the National Priorities List (NPL).

2. The Charge

The original charge to the Science Advisory Board (SAB) Subcommittee was to: "provide a technical review of the proposed guidance, evaluate consistency with other Agency programs, and provide guidance on the appropriateness and potential impact of the document. Specific issues include: a) technical considerations, such as colloidal mobility and transport mechanisms, phase changes, and fate and transport of inorganic contaminants; and b) policy issues, including guidance from other federal programs, and potential adverse impacts on other guidance or work in progress."

In this Appendix, the Subcommittee elaborates on the scientific principles that formed the basis of their letter report.

3. Background

The Agency uses groundwater monitoring data as part of the overall evaluation of whether or not a given site is listed on the NPL. Groundwater sampling techniques involve invasive practices (e.g., well drilling) which have the potential to alter the characteristics of the aquifer and the ground water. Hence, much care is required to obtain a groundwater sample that represents the metals present in the aquifer before the well was bored. Controversy has arisen in the technical community over the best sampling method and whether or not the sample should be filtered prior to analysis for metals.

Because of differences in the way wells are installed, differences in packing materials, and differences in the techniques used to collect groundwater samples, considerable variability in analytical results can occur between wells and from sample to sample. Filtering a sample is perceived by many individuals as an approach that eliminates suspended particles and some colloids[1], that contain metals (both those of natural origin and those derived from human activities) that would not normally be in the ground water if the soil or rock material were not disturbed during sampling. Under these conditions, filtering of groundwater samples is likely to yield a more representative sample and usually reduce the analytical variability between sampling events.

The literature cited by EPA indicates that colloids as large as 2 micrometers (µm) may be mobile in porous media (Puls and Powell, 1992) and that colloid concentrations can be as high as 1000 times higher in fractured granitic systems (McCarthy and Deguelde, 1993). Under these conditions, filtering is likely to yield less representative samples. Even in the situation where non-mobile colloids were known to be present in ground water samples, the process of filtering may remove mobile particles along with the non-mobile particles.

Hence, the question arises as to whether or not field filtered or non-filtered samples should be collected and whether one or the other is of greater value in judging the concentration of mobile metal in the undisturbed ground water. Citing the literature, the proposed guidance states that for properly constructed wells, the correct use of "low-flow" purging and sampling techniques results in samples that more accurately represent the mobile composition of ground waters. The low flow technique maximizes representativeness by:

a) minimizing disturbances that may suspend geochemical materials that are not usually mobile;

b) minimizing disturbances that may expose new reactive sites that could result in leaching or adsorption of inorganic constituents of ground water;

c) minimizing exposure of the ground water to the atmosphere or negative pressures, ensuring that the rate of purging and sampling doesn't remove ground water from the well at a rate much greater than the natural ground water influx; and

d) monitoring indicator parameters to identify when stagnant waters have been purged and the optimum time for sample collection has been reached.

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[1]A colloid is defined as a particle or particles having diameters of less than 10 µm (Puls and Powell, 1992).

In summary, based upon the ability of the low-flow sampling technique to collect representative samples, the Agency proposes that filtering of samples prior to metals analysis is usually not required.

4. Guiding Principles

There are many purposes for which ground water samples may be collected, and the specific purpose often dictates how the sample is collected, filtered, and analyzed. Under the conservative HRS system, data are used to evaluate the potential for contaminants to enter drinking water sources and become a potential source of human exposure. In this context, the Subcommittee suggests the following principles. These principles--like the proposed national guidance--may have a much broader application than that just applied to the HRS system.

a) The purpose for which the sample is being analyzed and the goals of the program should determine the sampling and analysis procedures.

b) Ground water samples should be collected and handled so that they are representative of the undisturbed aquifer.

c) Ideally, the sampling technique employed should be one that does not withdraw water at a rate that exceeds the recharge rate of the soil or rock. This means that in most cases a "slow pump" technique is preferred.

d) Scientific investigations indicate that in most cases the analytical results from high flow rate sampling with field filtering is similar to those obtained from unfiltered samples collected under slow pump rate conditions.

e) In aquifers that have a very slow rate of recharge, techniques other than slow pumping may be necessary and this may result in increased levels of suspended particles. In these, and some other cases, it may be necessary to filter the sample to remove solids that are introduced by the invasive well drilling and sampling techniques and to use the results accordingly.

fi It is inappropriate to filter ground water samples collected from aquifers that contain naturally occurring suspended particles if they result from transport through the aquifer due to the nature of the subsurface geology.

5. Major Recommendations

The Subcommittee agrees with OERR that for Superfund Site Assessments the low-flow sampling technique without filtration is the preferred sampling approach for subsequent metal analysis when well construction, well maintenance and hydrogeological conditions such as flow rate allow. Under such conditions, the collected

samples should represent these dissolved and particulate metals that are mobile in groundwater systems. The Agency s proposal to rely upon low flow sampling and unfiltered samples is a conservative approach that favors false positives over false negatives.

The Subcommittee recommends that the revised guidance clearly state that filtration may be required under conditions resulting in the suspension of geological or colloidal particulates that would not otherwise be mobile. For example, sampling from wells constructed in fine grained soils, wells with filter packs not matched to the geologic formations, or slow recharging wells may result in the suspension of particulate materials and associated metals that are not mobile in the groundwater system.

The Subcommittee considers that the Agency is the appropriate body to decide whether the national guidance should require filtered or unfiltered samples for metals analysis.

6. Elaboration of Recommendations

6.1 Purpose of the Analysis

Although the proposed guidance makes specific recommendations on handling groundwater samples for metal analysis, these recommendations are not intended to preclude different techniques being used to meet other project goals related to surface waters and organic chemicals; cf., report currently being prepared by the SAB's Ecological Processes and Effects Committee (EPEC). The Subcommittee recommends that the revised guidance clearly provide the flexibility to match sample handling techniques with the purpose of any study. For instance, numerous separation methods may be required to determine what fraction of a total concentration is biologically available.

Similarly, the Subcommittee recommends that the revised guidance indicate that it applies equally to site samples and background samples. To the extent possible, samples from the site and reference areas should be gathered and handled by identical methods.

6.2 When Filtering May be Appropriate

Situations in which filtered samples might be appropriate include the following:

a) When low flow sampling is greater than the rate of groundwater flow - This situation arises when a well is installed in a formation where the groundwater flow rate is much less than 0.1 liters per minute (L/min) through the cross sectional area of the well. This situation would be identified based on hydraulic conductivity estimates at the well (e.g., using baildown tests or grain size estimates) and the groundwater gradient in

the area. These are not field judgments and should be made prior to mobilizing the sampling crew.

The linear relationship between hydraulic conductivity (K, cm/sec), groundwater gradient (i, a dimensionless quantity), and the cross sectional area of a well screen (A) is given by:

$$\text{Flow Rate} = KiA \qquad (1)$$

Therefore, for even a relatively high hydraulic conductivity (e.g., K = .01 cm/sec), a relatively high gradient (i = 0.01), and a typical well screen (0.5 ft diameter and 5 ft long), the calculated flow rate of 0.014 L/min is much less than the 0.1 L/min referred to above.

$$A = (3.14) \times (6 \text{ in} \times 2.5 \text{ cm/in})^2 = \text{about } 700 \text{ cm}^2$$

$$\text{Flow Rate} = (.01 \text{ cm/sec}) \times (.01) \times 700 \text{ cm}^2 \times (60 \text{ sec/min}) \times (1 \text{ L}/1000 \text{ cc}) = 0.042 \text{ L/min}$$ -- which is 3x larger than the number in the table

b) When well construction is not matched to the formation being sampled - The well screen and filter pack are assumed to filter out the non-mobile fraction of the formation being sampled. This may not be the case for a well with a filter pack and slot size not matched to the formation. This can occur at wells installed without foreknowledge of the material to be encountered or when it is impractical to install a filter pack and slot size as small as would be required for a fine grained formation (Nielsen, 1995).

c) When local geochemistry is important - Filtering can be important when the geochemistry of the well environment mobilizes particulates in the vicinity of the well, that are not mobile outside the well filter pack and screen area. Although these situations may be much more difficult to identify, they and the potential need for filtering under such conditions should be recognized by the Agency in its proposed guidance.

6.3 Other Issues Affecting Samples

a) Well Construction - All wells used for sampling purposes should have design plans or recommended installation details. These plans or installation details should be made available to the Site Assessment Manager (SAM) prior to the sampling event. If possible a licensed well driller or an appropriate engineer or scientist should certify that the well was properly designed, located, and installed, in accordance with the site plan. This step will increase the confidence that the well was properly

installed and capable of yielding representative groundwater samples for analyses.

In cases where no documentation or certification of well design, construction, and installation exists, and the well yields samples that are turbid (>5 NTU), colored, cloudy, or contain suspended matter, the Subcommittee recommends that the sample be field filtered.

b) Well Stabilization - The Subcommittee has identified several places where the intended meaning of the proposed guidance is not clear in its discussion of indicators for determining when a well has stabilized and when sampling can occur. Specifically,

(1) The proposed guidance states that stabilization occurs when three stable consecutive measurements are made and comply with the acceptance criteria. Because this statement can be interpreted in several different ways, the revised guidance should specify how the criteria are to be applied. The table should explain what is intended and what is feasible for field activities. Questions such as the following arise from the current language. Do the criteria apply to the first and the third measurement? Do the criteria apply to consecutive pairs (the 1st to the 2nd measurement and the 2nd to the 3rd) such that a consistently increasing or decreasing trend is acceptable as long as the trend is less than the acceptance criteria as applied to consecutive pairs? Are the criteria applied to an average of the three measurements and the minimum and maximum? Are the acceptance criteria stated in terms of relative standard deviations for the three measurements?

(2) The Agency should review the acceptance criteria and ensure that they are appropriate over the range of measurements that can be encountered in the variable quality ground waters that may be sampled as part of site assessments. For example, if acceptance criteria may change as low concentrations of an indicator such as dissolved oxygen are measured, then separate acceptance criteria should be included for the separate ranges. For example, ± 3% is too stringent for an indicator such as dissolved oxygen (DO) measurements in anaerobic ground waters.

(3) The Agency should be careful in its use of terms such as "acceptable level" when discussing NTU (for example, on page 4 of the proposed guidance). What is meant by "acceptable levels in nephelometric turbidity units (NTU)"? Is this a reference to the 10 NTU criteria (page 7 of guidance) which when exceeded allows use of a 10 µm field filter? How does this criterion compare to the

RCRA SW-846 guidance(USEPA, 1995) "Samples containing greater than 5 NTU are only acceptable when well development is certified by a qualified hydro geologist as the best obtainable"? Does the limit of 10 NTU, (page 7 of the guidance) imply that mobile amounts of particulates/colloids cannot equal or exceed concentrations that yield NTUs of 5 or higher and that nephelometric measurements this high indicate that the samples were collected improperly? Is this true even when natural channeling occurs in fractured bedrock? What are the implications of such an upper limit?

Why does this section suggest use of temperature, pH and specific conductance when a nephelometer is not available? A reference cited by the guidance indicates that these parameters are insensitive to stabilization (Powell and Paul, 1992). Why not suggest indicator parameters (DO, redox potential) more sensitive to the establishment of stabilization?

c) Vertical Heterogeneity - The traditional purging of many well volumes with a bailer or high-speed pump prior to sampling is believed to have a side effect of vertically mixing and possibly averaging concentrations over the vertical water column that fell under the influence of purging. Low flow methods have been proposed as a method of collecting a more representative sample. When the pumping rate is less than the well recharge rate, the zone of influence over which averaging will occur is dramatically less and should be a function of pumping rates and ground water flow velocities. Tom Spittler of USEPA Region I, has found that substantial vertical VOC heterogeneity can be detected if discrete samples are collected throughout the water column. A reference cited by the guidance (Powell and Puls, 1993) also discusses vertical heterogeneity of inorganic contaminants. When vertical heterogeneity exists within a well and the rate of pumping is less than the recharge rate, the low-flow method's smaller zone of influence has the potential to result in variable measurements according to where the pump is located.

Therefore, assuming that the rate of pumping is less than the recharge rate and that the low-flow/no filtration method only samples a narrow horizontal zone, the Agency is faced with a number of questions:

(1) What is the likelihood for vertical heterogeneity to exist in a well with a 5' or 10' screen length?

(2) What are the objectives of a Superfund assessment? Are they for the average concentration across the entire screened length of the well or for the highest concentration?

(3) Where should the low-flow sampling point be placed? Middle of the screen? Bottom?

In summary, the Subcommittee recommends that unless there is evidence that vertical heterogeneity is not an issue, the guidance should include a cautionary note regarding the location of the low-flow sampling device when the pumping rate is less than the well's recharge rate.

d) LNAPLs and DNAPLs - The Subcommittee recommends that the Agency determine whether the low flow sampling method is appropriate when light or dense non-aqueous phase liquids (LNAPLs or DNAPLs) are present; the revised guidance should state the Agency's position on this issue. Region I suggests an alternate approach when LNAPL or DNAPL is present (Cohen and Mercer, 1993; USEPA, 1993).

e) Preserving Filtered Material - The Subcommittee recommends that the revised guidance include a paragraph that discusses disposition of the filtered material in those cases where field filtering is found to be necessary or preferable. For example, it may be advantageous to archive used filter media when assessments have the potential to be contentious or when questions remain regarding the ground water system of interest.[2] Should questions arise later about the propriety of filtration, the laboratory filter cake could be analyzed to explore the nature of the matter removed by the filter.

6.4 Consistency with Other Guidance

The Subcommittee reviewed a limited set of examples of existing guidance currently referenced by federal regulations and has found guidance which is not compatible with the proposed guidance for low flow/no filtering sampling of ground water for metals analysis. For example, Chapter 11 of SW-846 (US EPA, 1995)

a) Does not mention low flow sampling.

b) Recommends evacuation of 3 well volumes prior to sampling which is not in agreement with the minimum disturbance of low flow sampling.

c) Lists procedures for both dissolved (filtered) and total (non-filtered) metals and does not state a preference for either.

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[2] Almost all guidance recommends field filtering versus delayed filtering in the lab. One should not acid preserve a sample prior to filtering yet the longer you wait before preserving a sample the greater the possibility non-reversible changes will take place. However, at times samples are filtered in a lab since the lab is nearby or because the field environment will not allow for filtering.

Also, current Safe Drinking Water Act (SDWA) regulations (40 CFR 141.23) reference "Methods for Chemical Analysis of Water and Wastes " (US EPA, 1979) for metals analysis, which states "Drinking water samples containing suspended and settleable material should be prepared using the total recoverable metal procedure" (page METALS-5). The Agency's Contract Laboratory Program uses a similar digestion technique while the RCRA program uses a much more aggressive digestion procedure to determine "total" metals. RCRA Method 3005 is similar to the SDWA and the CLP digestion procedures but is referred to as "total recoverable or dissolved". This discrepancy in terms and sample preparation technique further complicates which components of ground water will be considered mobile by different programs.

Until such references are changed and terminology standardized, there will not be consistency across the different programs. Even if other existing guidance overrule these references, their continued presence will result in a lack of consistency as ground water sampling is applied across the various programs overseen by the Agency. However, this lack of consistency does not preclude the Agency from basing its decisions on sound scientific principles that are applicable to site assessments.

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U.S. Environmental Protection Agency
Science Advisory Board
Environmental Engineering Committee

Special Topics Subcommittee
April 29, 1997

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