The Regional Superfund Ground Water Forum is a group of ground-water scientists, representing EPA’s Regional Superfund Offices, organized to exchange up-to-date information related to ground-water remediation at Superfund sites.

Filtration of ground-water samples for metals analysis is an issue identified by the Forum as a concern of Superfund decision-makers. Inconsistency in EPA Superfund cleanup practices occurs where one EPA Region implements a remedial action based on unfiltered ground-water samples, while another Region may consider a similar site to be clean based on filtered ground-water samples. RSKERL-Ada and EMSL-Las Vegas have convened a technical committee of experts in the areas of ground-water geochemistry, inorganic chemistry, colloidal transport and ground-water sampling technology to examine this issue and provide technical guidance based on current scientific information.

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This document was written by Robert W. Puls and Michael J. Barcelona and edited by all members of the committee.

Filtration of ground-water samples for metals analyses will not provide accurate information concerning the mobility of metal contaminants. This is because some mobile species are likely to be removed by filtration before chemical analysis. Metal contaminants may move through fractured and porous media not only as dissolved species, but also as precipitated phases, polymeric species or adsorbed to inorganic or organic particles of colloidal dimensions. Colloids are generally considered as particles with diameters less than 10 microns (Stumm and Morgan, 1981). Numerous investigators have suggested the facilitated transport of contaminants in association with mobile colloidal particles. Kim et al. (1984) suggested that sorption to ground-water colloidal material caused the mobilization of some radionuclides in Gorleben ground waters. Saltelli et al. (1984) studied americium percolation in glauconitic sand columns and attributed the unretained fractions to migrating colloidal species.

Background/Support Information

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* Micron = mm = 10⁻⁶ meter

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These colloids were either homogeneous hydrous precipitates, or were formed from the adsorption of the radionuclide onto colloidal size mineral particles. Colloidal particles generated in batch experiments by Sheppard et al. (1979) were shown to adsorb significant quantities of radionuclides. Further work by Sheppard et al. (1980) concluded that the transport of radionuclides by colloidal clay particles must be considered in any contaminant transport model. Champlin and Eichholz (1968) showed that the movement of radioactive sodium and ruthenium in sand beds was associated with particulate matter of micron dimensions. Gschwend and Reynolds (1987) demonstrated that submicron ferrous phosphate colloids were suspended and presumably mobile in a sand and gravel aquifer.

Studies by Yao et al. (1971) and O'Melia (1980) indicate that colloidal particles in the range 0.1 to 1.0 micron may be most mobile in a sandy, porous medium. Kovenya et al. (1972) concluded that particles in the range 0.1 to 0.5 mm were most mobile in soil column studies. As much as 200 ppb copper, lead and cadmium was found associated with colloidal material in size range 0.015-0.450 mm by Tillekeratne et al. (1986). Rapid transport of plutonium (Pu) in core column studies by Champ et al. (1982) was attributed to colloidal transport, with 48% of the Pu associated with colloids in the size range 0.003-0.050 mm and 23% in the range 0.050-0.450 mm. Reynolds (1985) using carboxylated polystyrene beads ranging from 0.10 to 0.91 mm in size, recovered 45% of the 0.91 mm size beads, and greater than 70% of 0.10 and 0.28 mm size beads in laboratory sand column effluents.

Lake and estuarine studies by Baker et al. (1986) and Means and Wijayaratne (1982) demonstrated the importance of natural colloidal material in the transport of hydrophobic contaminants. Carter and Suffet (1982) found that a significant fraction of “dissolved” DDT in surface waters was bound to colloidal humic material. Takayanagi and Wong (1984) found over 70% of the total inorganic colloidal particles.

Analytical methods used to determine “dissolved” metal concentrations have historically used 0.45 micron filters to separate dissolved and particulate phases. If the purpose of such determinations is an evaluation of “mobile” species in solution, significant underestimations of mobility may result, due to colloidal associations. On the other hand, if the purpose of such filtration is to determine truly dissolved aqueous species, the passage of colloidal material less than 0.45 microns in size may result in the overestimation of dissolved concentrations (Bergseth, 1983; Kim et al. 1984; Wagemann and Brunskill, 1975). Kennedy et al. (1974) found errors of an order of magnitude or more in the determination of dissolved concentrations of aluminum, iron, manganese and titanium using 0.45 micron filtration. Sources of error were attributed to filter passage of fine-grained clay particles. Additionally, filtration of anoxic ground-water samples is very difficult without iron oxidation and colloid formation, causing a removal of previously dissolved species to be filtered. Filter loading and clogging of pores with fine particles may also occur, reducing the nominal size (Danielsson, 1981). Filtration should be viewed as only one approach for determining the “true” solution geochemistry of ground water, and others should be applied whenever possible.

### Purpose of Sampling

It is important to identify the purpose of ground-water sampling before decisions regarding filtration, centrifugation or other phase separation techniques are made. Is it to determine the mobility of contaminants or to determine in situ aqueous geochemistry? The following definitions are also useful for consideration of this issue:

1. **Total Contaminant Load Per Unit Volume of Aquifer** = **Mobile** + **Immobile Species**
2. **Mobile Species** = **Dissolved** + **Suspended Species**
3. **Dissolved** = **Free Ions** + **Inorganic Complexes** + **Low Molecular Weight Organic Complexes**
4. **Suspended** = **Adsorbed** + **Precipitated** + **Polymeric** + **High Molecular Weight Organic Complexes**

For an assessment of mobility, all mobile species must be considered, including suspended particles acting as adsorbents for contaminants. While not all suspended species may necessarily be sufficiently mobile or toxic to pose a health risk, a conservative approach is proposed at this time until more definitive data are available. Contaminant transport models which account for an additional aqueous mobile colloidal phase have been proposed by Avogadro and DeMarsily (1984) and Enfield and Bengston (1988).

A principle objective in a sampling effort for testing a geochemical speciation model is to obtain estimates of the free ion activities of the major and trace elements of interest. Since there are relatively few easily performed analytical procedures for making these experimental estimates, an alternative procedure is to test the analytically determined dissolved concentrations with model predictions including both free and complexed species. More and more remedial investigations are utilizing such models to make predictions about contaminant behavior based on dissolved concentrations. It is not the purpose of this report to suggest how to perform these analytical determinations, but as noted above, the use of a 0.45 micron filter as the operational definition of “dissolved” may be inappropriate. Analytical techniques such as ion selective electrodes, ion exchange and polarography may be more accurate. Research utilizing these and other techniques to correlate “dissolved” with filter size is recommended.

If one adopts the conservative approach with no filtration for contaminant mobility estimations, increased importance is placed on proper well construction, and purging and sampling procedures to eliminate or minimize sources of sampling artifacts.

### Sources of Sampling Artifacts vs. “real” Ground-water Environment

The disturbance of the subsurface environment as a result of well construction and sampling procedures presents serious
obstacles to the interpretation of ground-water quality results. Some degree of disturbance of natural conditions is inevitable. However, the impact of improper well construction and sampling techniques can permanently bias the usefulness and integrity of wells as sampling points. Several aspects of well construction and sampling procedures must be carefully considered to avoid errors associated with the introduction of foreign particles or the alteration of ambient subsurface conditions which may affect natural dissolved or suspended materials.

**Well Construction**

The design, drilling, and construction of monitoring wells have been identified as particularly important steps in the collection of representative water chemistry and hydrologic data. Several references have emphasized the minimization of both the disturbance and the introduction of foreign materials (USEPA, OSWER-9950.1, 1986; Barcelona, et al., 1983; Barcelona et al., 1985) because of the potential impact on water chemistry. The RCRA Technical Enforcement Guidance Document (USEPA, OSWER-9950.1, 1986) suggests that the well must allow for sufficient ground-water flow for sampling, minimize passage of formation materials into the well, and exhibit sufficient structural integrity to prevent collapse of the intake structure. It should be recognized, however, that the well must first provide a representative hydraulic connection to the geologic formation of interest. Without the assurance of this hydraulic integrity, the water chemistry information cannot be interpreted in relation to the dynamics of the flow system or the transport of chemical constituents.

More specific guidance is therefore necessary to maintain or restore the natural hydraulic conductivity of the formation in the vicinity of the screened portion of monitoring wells through the drilling, construction and development procedures. The literature on water well technology can be most helpful in this regard since minimal disturbances of the subsurface is a common goal in maximizing both the yield of water supply wells and the representativeness of water samples and hydraulic information from monitoring wells (Driscoll, 1986).

To insure the long-term integrity of monitoring wells, particularly with respect to excluding foreign particles and permitting the passage of mobile (i.e., dissolved and suspended) contaminants, specific items which should be observed are:

1) If no alternative to the use of drilling muds or fluids exists, these materials must be removed from the well bore and adjacent formations by careful well development (Driscoll, 1986). This guidance also applies to the removal of the low permeability “skin” which is caused by abrasion, oxidation and invasive muds which may seal the well bore from the screened interval and bias in situ determinations of hydraulic conductivity (Faust and Mercer, 1984; Moench and Hsieh, 1985; Faust and Mercer, 1985). Pumping rates during development should be documented and care should be taken not to exceed these rates during purging or sampling since further development and well damage may aggravate suspended particulate and turbidity problems even in properly designed wells.

2) The emplacement of grouts and seals to isolate the screened interval must be carefully done. The use of tremie pipes and frequent checking of the depth of emplacement of clay or cement grouts during well construction are strongly encouraged.

It is also important to take care to follow manufacturer's guidelines on the hydration of cement or expanding cement as grouts or seals. Excess water addition and grading of cement components or materials due to free fall through standing water can permanently damage the well's integrity (Evans and Ellingson, 1988).

3) Casing and screen materials must be selected to retain their integrity in the subsurface environment (i.e., avoid iron, steel), minimize bias to water samples and insure that screen openings are not reduced by the buildup of corrosion products or by compression (USEPA, OSWER-9950.1, 1986). These effects can be checked by repeat determinations of in situ hydraulic conductivity over the useful life of the well. Redevelopment and replacement of the well should be considered if deterioration or significant changes in hydraulic conductivity are observed. Erratic water level readings and sudden changes in turbidity or purging behavior of monitoring wells prior to sampling are warning signs of possible loss of material integrity.

4) Well design fundamentals with regard to the selection of a filter pack and screen size are among the most important issues in obtaining representative hydraulic and water quality information. The exclusion of fines, clays, and silts can be achieved by selecting the grain-size distribution for the filter pack by multiplying the 50-percent retained size of the finest formation sample by a factor of two (Driscoll, 1986). The filter pack material should be cleaned and washed free of fines to insure that extraneous contaminants or particles are removed. The well screen slot openings should be chosen to retain 90% of the filter pack material after development. In natural packed wells it may be advisable to select a screen slot size which will retain at least 50% of the finest material in the screened interval. Minimizing slot screen width however, often leads to greater time and energy spent in well development. The need to document well development procedures cannot be overemphasized.

Maintenance of the hydraulic performance of monitoring wells and the connection of wells to the zones of greatest hydraulic conductivity, where contaminant transport is most probable, should take equal importance to the collection of representative water quality data.

**Purging and Sampling**

Water that remains in the well casing between sampling periods is unrepresentative of water in the formation opposite the screened interval. It must be removed by purging or isolated from the collected sample by a packer arrangement prior to the collection of representative water samples. Water level readings must be made carefully to avoid the disturbance of fines or precipitates which may enter or form in the well due to chemical reactions or microbial processes and accumulate on the interior walls of the well casing screen or at the bottom of the well.
Similarly, it is important to purge the stagnant water at flow rates below those used in development to avoid further development, well damage or the disturbance of accumulated corrosion or reaction products in the well. The use of certain sampling devices, particularly bailers and air-lift arrangements, should be discouraged in order to avoid the entrainment of suspended materials which are not representative of mobile chemical constituents in the formation of interest.

A note of caution should be voiced to encourage repetitive sampling of monitoring wells prior to judging the representativeness of determinations of hydraulic conductivity, water level readings and water quality data. The effects of the inevitable "trauma" due to drilling, sealing and development of monitoring wells can bias observations of water chemistry until the subsurface is allowed to equilibrate sufficiently (Walker, 1983). Estimates of the time to achieve equilibration vary substantially, particularly when drilling fluids are used in highly permeable formations (Brobst, 1984; Driscoll, 1986); however, periods of weeks to several months may be necessary before even major ionic constituents of ground water equilibrate to previous levels (Barcelona, et al., 1988).

Recommendations for Sampling

In general, the zone of interest must be isolated, the sample pumped slowly to minimize turbidity and sample collected in such manner as to eliminate O2 and CO2 exchange with the atmosphere. No filtration for mobile metals determination is recommended. If the unfiltered values exceed maximum contaminant level concentrations for ground-water quality, additional analyses and re-evaluation of sampling artifacts are required. It should be emphasized that extreme differences between unfiltered and 0.45 mm filtered samples does not preclude the use of unfiltered data for risk assessment decisions. Significant particulate mobility may be occurring at such a site, and additional analyses with other larger filters (e.g., >0.45 mm) may be most appropriate given the current size estimates for upper limits for mobile particles.

Isolation of Sampling Zone

Isolation of the sampling zone is necessary to minimize the purge volume as well as to minimize air contact. This is especially important since Eh/pH conditions of the formation waters are notoriously sensitive to dissolved gases content. Inflatable packers can be used to achieve isolation of the sampling zone.

Pumping for Sample Collection

It is recommended that a positive displacement pump can be used. Other types of sample collection (e.g., bailing) may cause displacement of non-mobile particles or significantly alter ground water chemistry leading to colloid formation (e.g., vacuum pumps). Surging must be avoided, and a flow rate as close to the actual ground-water flow rate should be employed. Acknowledging that this may be impossible or impractical in some instances, a pumping flow rate based on the linear ground-water flow rate and open screen area is proposed, where

\[
\text{pumping flow rate} = \text{linear GW flow rate} \times 2 \times \text{screen ht.} \times \text{well radius} \times 10
\]

While an initial approximation, flow rates around 100 ml/min have been used to successfully sample ground-waters in a quiescent mode.

Additional research is needed in this area, particularly with respect to the appropriateness of this generic equation. An inexpensive flow-through type cell set-up utilizing this approach was described by Garske and Schock (1986).

Assessment of Water Constituents While Sampling

Monitoring of the pumped ground water for dissolved oxygen, temperature, conductivity and pH aids in the interpretation or establishment of ground-water background quality. Gschwend and co-workers (personal communication) have observed that turbidity diminished dramatically after prolonged pumping, changing similarly, although possibly more slowly, than other water quality parameters (e.g., O2, conductivity). An initial estimate proposed for time of pumping necessary to collect water from a formation is around two times the time required to get plateau values for the above parameters.

No Filtration for Mobile Fraction Determination

Those samples intended to indicate the mobile substance load should not be filtered. Steps to preserve their integrity, such as acidification, should be performed as soon as possible.

Filtration for Specific Geochemical Information

Any filtration for estimates of dissolved subsurface species loads should be performed in the field with no air contact and immediate preservation and storage. In-line pressure filtration is best with as small a filter pore size as practically possible (e.g., 0.05, 0.10 micron). Using a smaller pore size filter will require longer sample collection time, increasing the need for air exclusion from the sample (Laxen and Chandler, 1982; Holm et al., 1988). Polycarbonate membrane-type filters with uniform and sharp size cutoffs are recommended to minimize particle loading on the filter. Although membrane filters are more prone to clogging than fiber-type filters, the uniform pore size, ease of cleaning, and minimization of adsorptive losses from the sample tend to improve the precision and accuracy in the analytical data. The filter holder should be of material compatible with the metals of interest. Holders made of steel are subject to corrosion and may introduce non-formation metals to samples. Large diameter filter holders (e.g., > 47 mm) are recommended to reduce clogging and pore size reduction and for ease of filter pad replacement. The use of disposable in-line filters are suggested for convenience if of sufficient quality. Prewashing of filters should be routinely performed. Work by Jay (1985) shows that virtually all filters require prewashing to avoid sample contamination.

Quality assurance and quality control becomes increasingly important when adopting the above recommendations. The use
of field blanks and standards for field sampling is essential. Field blanks and standards enable quantitative correction for bias due to collection, storage and transport. Analysis of the filters themselves and their particulate load is suggested as a check on mass balance and filtration effects on solid/solution separation efficiency.

References


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