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Project Summary

Practical Guide for Ground-Water Sampling

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This work was initiated as the second phase of an investigation of the reliability of monitoring well construction and ground-water sampling techniques. The project also included both laboratory and field testing of sampling materials and sampling mechanisms with an emphasis on minimizing error, particularly for volatile organic compound sampling and analysis. The Guide is a companion volume to the Phase 1 report, "A Guide to the Selection of Materials for Monitoring Well Construction and Ground-Water Sampling," (EPA/600/2-83/024).

The full report explains the need to address the quality control and quality assurance considerations of a ground-water monitoring program at the outset of planning. The sampling and analytical protocols for specific monitoring installations should be integrated into a well conceived design for the collection of high quality hydrologic and chemical data. Though accuracy and precision data provide measures of data quality, it is equally important to collect samples that are representative of *in situ* conditions. These goals can be achieved if the essential elements of a ground-water sampling program are addressed in the preliminary and implementation phases of monitoring program development.

The essential elements of effective ground-water sampling include:

- **Evaluation of the hydrogeologic setting and program information needs,**
- **Proper placement and construction of the well,**
- **Evaluation of performance of the well and purging strategies, and**
- **The design and execution of sampling and analytical protocols which entail appropriate selection of sampling mechanisms and materials as well as sample collection, handling and analysis procedures.**

Detailed discussions of the advantages and disadvantages of various approaches to selecting appropriate methods and materials for specific monitoring purposes are provided in the Guide. The emphasis is on straightforward techniques which minimize both the disturbance of the subsurface environment and the potential sources of error for routine sampling applications. Further, specific recommendations are made for step-by-step sampling protocols which should be applied in sampling for volatile organic compounds which are among the most difficult chemical constituents to sample effectively. The recommendations are supported by extensive references, where the literature permits, and it should prove useful to the planning and execution of regulatory and research activities which demand high quality ground-water quality data.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, and the Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Ground-water monitoring is conducted for a variety of purposes, though detective and assessment compliance monitoring efforts are most common. The absence of proven recommendations for effective monitoring network designs and reliable sampling protocols has resulted in the collection of ground-water quality data with questionable value. When this type of data is used as a basis for assessment or remedial action activities, the success of these actions may be very limited.

Recent research has demonstrated that the details of well construction, choice of sampling mechanisms and materials and sampling protocols can introduce errors into analytical results which exceed those involved in the analytical procedures. Analytical operations have been the major focus of quality assurance and quality control (QA/AC) recommendations for monitoring programs. Sampling QA/AC is equally important to the development of high quality data which is representative of the site under investigation. Requiring that water samples be representative of the *in situ* condition is insufficient to ensure a high level of confidence in the monitoring results. The hydraulic performance of the well (i.e., sampling point) and the integrity of the sampling protocol must be established before samples are collected, if representative data are to be generated. Then the characteristics of a representative sample can be established for the specific goals of the program.

The Guide provides a thorough discussion of the essential elements of well construction and sampling protocols for the collection of high quality ground-water quality data. Representative water samples are generally defined by being minimally disturbed samples which satisfy charge balance considerations and permit the determination of trace organic compounds at their limits of quantitation within acceptable accuracy and precision limits. Each element of the sampling protocol for a particular investigation can be evaluated for its contribution to error in the final results.

The available literature supports the approach that a representative sampling protocol for volatile or reactive chemical constituents can satisfy the most demanding data quality requirements applied to routine monitoring efforts. Sampling and analytical protocol development must be tailored to the actual hydrogeologic conditions of the site under investigation. Careful attention to the elements of the sampling protocol will permit the refinement of routine procedures as the monitoring activity develops. The emphasis of the recommendations is on the simplest sampling procedures possible which provide data of known quality over the duration of the monitoring effort.

Hydrogeologic Setting and Information Requirements

The hydrogeologic conditions at each site (e.g., background and regulated unit) must be evaluated for the potential impacts the setting may have on the development of the monitoring program and the quality of the resulting data. The types and distribution of geologic materials, the occurrence and movement of ground water through those materials, the location of the site in the regional ground-water flow system, the relative permeability of the materials and the potential interactions between the mineral and biological constituents of the formations of interest, and the chemical constituents of interest must all be considered. Both the direction and the rate of ground-water movement are important. Piezometric surface data or water level information on each geologic formation at properly selected locations will provide the basis for determining horizontal and vertical ground-water flow paths at the site. There are significant differences between the hydrogeology of arid and humid climatic regions, as well as seasonal variations which should be taken into account. The rate of ground-water travel can be used to calculate optimum sampling frequencies, should additional detail beyond that provided in quarterly sampling become necessary.

Additional site and waste information needs arise when tailoring the sampling and analytical protocols to the specific needs of the program. A minimum data set for ground-water monitoring should include general water quality parameters, hydrologic parameters and pollutant indicator parameters. A suggested list of basic measurements is provided below:

Chemical Parameters

pH, Ω^{-1}, TOC, TOX
Alkalinity, Cl^-, NO_3^-, $SO_4^=$, $PO_4^{\equiv}$, silicate
Na^+, K^+, Ca^{++}, Mg^{++}, Fe and Mn

Hydrologic Parameters

Water Level, hydraulic conductivity

The pollutant indicator parameters noted above [i.e., pH, Ω^{-1}, (specific conductance), TOC and TOX] provide minimal capability to ensure the detection of target chemical constituents in ground water. The pH and conductance parameters should be measured with care in the field. TOC and TOX determinations should be made after collection in headspace-free glass vials with Teflon®* septa to preserve the volatile organic fraction of the dissolved organic matter. The pollutant indicator parameters should also be supplemented with determinations of specific chemical constituents which are likely to be mobile and persistent in the subsurface.

Well Placement and Construction Procedures

The placement and construction of monitoring wells are among the most difficult tasks involved in developing an effective monitoring program. The preliminary locations and depths of monitoring wells should be selected on the basis of the best available pre-drilling information. Then, as the installation of these wells progresses, new geologic and hydrologic data should be incorporated into the overall monitoring plan to ensure that the wells will perform the tasks for which they are designed. It is advisable to select initially a minimum array of monitoring wells for the collection of geologic and hydrologic data. Additional wells can be positioned later at monitoring points likely to intercept contaminant flow paths.

Well construction should be accomplished with minimal disturbance of the subsurface. The selection and cleaning of both drilling equipment and well construction materials should be performed with the aim of minimizing the introduction of foreign materials into the subsurface environment. Given the relatively shallow depths of interest in many ground-water monitoring efforts, hollow-stem auger drilling techniques are preferred because they are mobile, fast, and inexpensive. Also, disturbance of the subsurface can be effectively minimized. To properly define the movement of pollutants, in both vertical and horizontal directions, it is essential to collect depth discrete water level data. Well completion depth will depend on the location of the uppermost permeable, saturated zone (i.e., "water-table") in unconfined formations or the piezometric surface of the most shallow permeable zone in confined formations. Vertically nested wells provide information on the vertical direction of ground-water movement and their placement will be a function of the hydrogeologic setting, particularly the relative horizontal and vertical permeabilities of the formations beneath the site. Screen size, grouts, seals and sampling point

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use documentation are also important aspects of monitoring well construction which should be addressed in the monitoring program.

Evaluation of Well Performance

The effectiveness of a ground-water monitoring program may be judged on the attention which has been paid to the evaluation of the hydraulic performance of the monitoring well network. Each well should be properly developed after construction and periodically redeveloped to ensure that it provides useful hydraulic data. Development also reduces the time and effort necessary to collect representative ground-water quality information. A variety of proven well development techniques are amenable to the development of shallow 2" o.d. monitoring wells. Accurate water level measurements provide the primary data for the evaluation of well performance. Steel tapes (graduated to the nearest hundredth of a foot with raised lettering and divisions), electrical drop lines and sensitive pressure transducers are useful tools in this regard.

Field hydraulic conductivity testing of the monitoring wells will avoid the unresolved issues which attend the interpretation of laboratory conductivity test results. Slug or bail tests, repeated at least three times, should provide accurate hydraulic conductivity determinations with a precision of ±20%. In general, multiple pump tests are too expensive to consider for evaluating the hydraulic performance of all monitoring wells within a site network. The results of conductivity tests provide a basic measure of well hydraulic well performance which is useful for judging the significance of water level excursions and long-term well performance. The testing procedures should be repeated at least every five years and after each redevelopment effort is performed. Well performance evaluation also provides a basis for determining an appropriate well purging strategy prior to sampling. No single number of purge volumes to be pumped prior to sampling can be expected to suit all situations. A well conceived purging strategy that includes pumping rates and volumes calculated on the basis of well performance and the transmissivity of the formation of interest is essential to effective ground-water sampling efforts.

Sampling Protocol

The hydraulic performance of the sampling points permits the design and execution of effective water sampling and analytical protocols. These protocols should be planned for collecting verifiably high quality water chemistry results in order to distinguish natural variability in the geochemistry of the subsurface from those caused by site operations. The sampling protocol should incorporate sampling mechanisms and materials that are appropriate for the information needs of the program. Since contaminant migration may be detected at trace (e.g., ppb) levels of individual constituents, sampling mechanisms and materials must be very carefully chosen to avoid biases caused by contamination or sorption. The materials of well construction, samplers and sample transfer tubing are as important as sample storage vessels and analytical performance in this respect. Recommended materials for well construction and sampling devices are shown in Tables 1 and 2. Materials' selections should be made with the long-term use of the sampling points in mind.

Sampling mechanisms are devices for the collection of water samples. They are not, of themselves, sampling methods. This should be clear from inspection of Figure 1. The steps in the sampling protocol in the first column of the figure are common to all ground-water monitoring efforts. Though the details of individual monitoring efforts may vary, the steps in Figure 1 provide a guide for effective planning. The performance of the sampling point, materials selected and the chemical constituents of interest will dictate the choice of appropriate sampling devices. Figure 2 contains *recommendations for sampling mechanisms* according to the specific demands of the monitoring effort.

Conclusions

The development of reliable sampling protocols for ground-water quality monitoring is a complex, programmatic process that must be designed to meet the specific

Table 1. *Recommendations for Rigid Materials in Sampling Applications (In Decreasing Order of Preference)*

Material	*Recommendations*
Teflon® *(flush threaded)*	*Recommended for most monitoring situations with detailed organic analytical needs, particularly for aggressive, organic leachate impacted hydrogeologic conditions. Virtually an ideal material for corrosive situations where inorganic contaminants are of interest.*
Stainless Steel 316 *(flush threaded)*	*Recommended for most monitoring situations with detailed organic analytical needs, particularly for aggressive, organic leachate impacted hydrogeologic conditions.*
Stainless Steel 304 *(flush threaded)*	*May be prone to slow pitting corrosion in contact with acidic high total dissolved solids aqueous solutions. Corrosion products limited mainly to Fe and possibly Cr and Ni.*
PVC *(flush threaded)* *other noncemented connections, only NSF* approved materials for well casing or potable water applications*	*Recommended for limited monitoring situations where inorganic contaminants are of interest and it is known that aggressive organic leachate mixtures will not be contacted. Cemented installations have caused documented interferences.* *The potential for interaction and interferences from PVC well casing in contact with aggressive aqueous organic mixtures is difficult to predict. PVC is not recommended for detailed organic analytical schemes.*
	Recommended for monitoring inorganic contaminants in corrosive, acidic inorganic situations. May release Sn or Sb compounds from the original heat stabilizers in the formulation after long exposures.
Low-Carbon Steel *Galvanized Steel* *Carbon Steel*	*May be superior to PVC for exposures to aggressive aqueous organic mixtures. These materials must be very carefully cleaned to remove oily manufacturing residues. Corrosion is likely in high dissolved solids, acidic environments, and particularly when sulfides are present. Products of corrosion are mainly Fe and Mn, except for galvanized steel which may release Zn and Cd. Weathered steel surfaces present very active adsorption sites for trace organic and inorganic chemical species.*

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** National Sanitation Foundation approved materials carry the NSF logo indicative of the product's certification of meeting industry standards for performance and formulation purity.*

Table 2. *Recommendations for Flexible Materials in Sampling Applications (In Decreasing Order of Preference)*

Materials	*Recommendations*
Teflon®	*Recommended for most monitoring work, particularly for detailed organic analytical schemes. The material least likely to introduce significant sampling bias or imprecision. The easiest material to clean in order to prevent cross-contamination.*
Polypropylene *Polyethylene (linear)*	*Strongly recommended for corrosive high dissolved solids solutions. Less likely to introduce significant bias into analytical results than polymer formulations (PVC) or other flexible materials with the exception of Teflon®.*
PVC (flexible)	*Not recommended for detailed organic analytical schemes. Plasticizers and stabilizers make up a sizable percentage of the material by weight as long as it remains flexible. Documented interferences are likely with several priority pollutant classes.*
Viton® *Silicone (medical grade only)* *Neoprene*	*Flexible elastomeric materials for gaskets, O-rings, bladder and tubing applications. Performance expected to be a function of exposure type and the order of chemical resistance as shown. Recommended only when a more suitable material is not available for the specific use. Actual controlled exposure trials may be useful in assessing the potential for analytical bias.*

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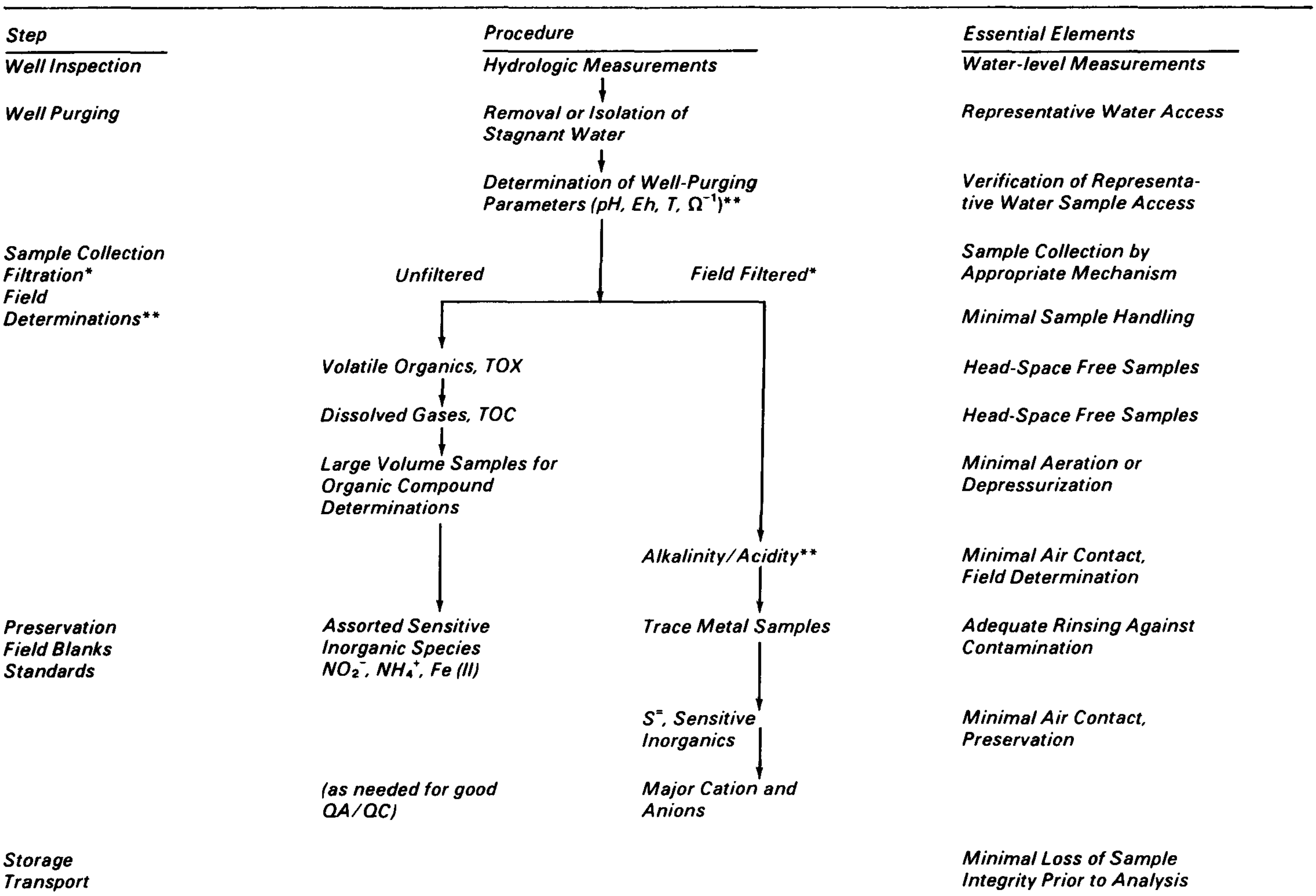
goals of the monitoring effort in question. The long-term goals and information needs of the monitoring program must first be thoroughly understood. Once these considerations have been identified, the many factors that can affect the results can be addressed.

In formulating the sampling protocol, the emphasis should be to collect hydrologic and chemical data that accurately represent *in situ* hydrologic and chemical conditions. With good quality assurance guidelines and quality control measures, the protocol should provide the needed data for successful management of the monitoring program at a high level of confidence. Straightforward techniques that minimize the disturbance of the subsurface and the samples at each step in the sampling effort should be given priority.

The planning of a monitoring program should be a staged effort designed to collect information during the exploratory or initial stages of the program. Information gained throughout the development of the program should be used for refining the preliminary program design. During all phases of protocol development, the long-term costs of collecting the required hydrologic and chemical data should be kept in mind. These long-term costs may be several orders of magnitude larger than the combined costs of planning, well construction, purchase of sampling and support equipment, and data collection start-up. It also should be remembered that high quality data cannot be obtained from a poorly conceived and implemented monitoring program, regardless of the added care and costs of sophisticated sampling and analytical procedures.

Finally, the ultimate costs of defending poor quality data in court or in compliance to regulatory requirements should not be overlooked. Due to the lack of documented standard techniques for developing monitoring programs, constructing monitoring wells, and collecting samples, quality control measures must be tailored for each individual site to be monitored. They should be designed to ensure that disturbances to both the hydrogeologic system and the sample are minimized. The care exercised in the well placement and construction, and sample collection and analysis can pay real dividends in the control of systematic errors. Repeated sampling and field measurements will further define the magnitude of random errors induced by field conditions and human error. The burden of assuring the success of a program relies on careful documentation and the performance of quality assurance audit procedures.



*Denotes samples that should be filtered in order to determine dissolved constituents. Filtration should be accomplished preferably with in-line filters and pump pressure or by N_2 pressure methods. Samples for dissolved gases or volatile organics should not be filtered. In instances where well development procedures do not allow for turbidity-free samples and may bias analytical results, split samples should be spiked with standards before filtration. Both spiked samples and regular samples should be analyzed to determine recoveries from both types of handling.

**Denotes analytical determinations which should be made in the field.

Figure 1. *Generalized flow diagram of ground-water sampling steps.*

← Increasing Reliability of Sampling Mechanisms

Increasing Sample Sensitivity ↑

Type of Constituent	*Example of Constituent*	*Positive Displacement Bladder Pumps*	*Thief, in situ or Dual Check Valve Bailers*	*Mechanical Positive Displacement Pumps*	*Gas-Drive Devices*	*Suction Mechanisms*
Volatile Organic Compounds *Organometallics*	*Chloroform* *TOX* CH_3Hg	*Superior Performance for Most Applications*	*May be adequate if well purging is assured*	*May be adequate if design and operation are controlled*	*Not recommended*	*Not recommended*
Dissolved Gases *Well-Purging Parameters*	O_2, CO_2 *pH*, Ω^{-1} *Eh*	*Superior Performance for Most Applications*	*May be adequate if well purging is assured*	*May be adequate if design and operation are controlled*	*Not recommended*	*Not recommended*
Trace Inorganic Metal Species *Reduced Species*	*Fe, Cu* NO_2^-, $S^=$	*Superior Performance for Most Applications*	*May be adequate if well purging is assured*	*Adequate*	*May be adequate*	*May be adequate if materials are appropriate*
Major Cations & Anions	Na^+, K^+, Ca^{++} Mg^{++}	*Superior Performance for Most Applications*	*Adequate*	*Adequate*	*Adequate*	*Adequate*
	Cl^-, $SO_4^=$		*May be adequate if well purging is assured*			

Figure 2. *Matrix of sensitive chemical constituents and various sampling mechanisms.*

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The complete report, entitled "Practical Guide for Ground-Water Sampling," (Order No. PB 86-137 304/AS; Cost: $16.95, subject to change) will be available only from:

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