ENHANCEMENTS OF NONPOINT-SOURCE MONITORING PROGRAMS TO ASSESS VOLATILE ORGANIC COMPOUNDS IN GROUND WATER OF THE UNITED STATES

Wayne W. Lapham, Michael J. Moran, and John S. Zogorski

ABSTRACT

The U.S. Geological Survey (USGS) has compiled a national retrospective data set of analyses of volatile organic compounds (VOCs) in ground water of the United States. The data are from Federal, State, and local nonpoint-source monitoring programs, collected between 1985-95. This data set is being used to augment data collected by the USGS National Water-Quality Assessment (NAWQA) Program to ascertain the occurrence of VOCs in ground water nationwide. Eleven attributes of the retrospective data set were evaluated to determine the suitability of the data to augment NAWQA data in answering occurrence questions of varying complexity. These 11 attributes are the VOC analyte list and the associated reporting levels for each VOC, well type, well-casing material, type of openings in the interval (screened interval or open hole), well depth, depth to the top and bottom of the open interval(s), depth to water level in the well, aquifer type (confined or unconfined), and aquifer lithology. VOCs frequently analyzed included solvents, industrial reagents, and refrigerants, but other VOCs of current interest were not frequently analyzed.

About 70 percent of the sampled wells have the type of well documented in the data set, and about 74 percent have well depth documented. However, the data set generally lacks documentation of other characteristics, such as well-casing material, information about the screened or open interval(s), depth to water level in the well, and aquifer type and lithology. For example, only about 20 percent of the wells include information on depth to water level in the well and only about 14 percent of the wells include information about aquifer type.

The three most important enhancements to VOC data collected in nonpoint-source monitoring programs for use in a national assessment of VOC occurrence in ground water would be an expanded VOC analyte list, recording the reporting level for each

analyte for every analysis, and recording key ancillary information about each well. These enhancements would greatly increase the usefulness of VOC data in addressing complex occurrence questions, such as those that seek to explain the reasons for VOC occurrence and nonoccurrence in ground water of the United States.

INTRODUCTION

Background

In 1991, the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program began full-scale implementation. The long-term goals of the NAWQA Program are to describe the status and trends in the quality of a large representative part of the surface-water and ground-water resources of the United States (U.S.) and to provide an improved understanding of the primary natural and human factors that affect the quality of these resources. The NAWQA Program has two major operational components (Gilliom et al., 1995): (1) hydrologic investigations of large river basins and aquifer systems, referred to as Study-Unit Investigations, and (2) a National Synthesis that summarizes results from NAWQA studies with information from other programs, agencies, and researchers to produce regional and national assessments for priority water-quality issues. National Synthesis studies of nutrients and pesticides began in 1991, a study of volatile organic compounds (VOCs) began in 1994, and studies of trace elements and ecology began in 1999.

VOCs were selected for National Synthesis because of the occurrence of this constituent group in many of the water supplies in the U.S. (Office of Technology Assessment 1984; Tennant et al., 1992; Pankow and Cherry, 1996). Over the long term, a national assessment of the occurrence, status, and distribution of VOCs in ground water will rely to a large extent on data collected by NAWQA Study Units (Lapham and Tadayon, 1996; Gilliom et al., 1995). To augment the national assessment, VOC National Synthesis is compiling a 'Ground Water VOC Retrospective Data Set' using data collected from nonpoint-source ground-water-quality monitoring networks established by USGS and by other Federal, State, and local agencies (Lapham et al., 1997). The locations of supplemental coverage include areas in NAWQA Study Units that have not been sampled to date (1999) and areas outside of the NAWQA Study Units.

Compilation of the Ground Water VOC Retrospective Data Set

The retrospective data described and summarized in this article were compiled during 1995-96 by NAWQA Study Units and the VOC National Synthesis in cooperation with Federal, State, and local agencies. Criteria for selection of retrospective data required that a minimum amount of information be known about each sample before inclusion in the data set (Lapham and Tadayon, 1996, table 5). Minimum data requirements were that: (1) National methods for collection and analysis of VOCs were used and that the analytical method and method detection limits or the reporting levels for each VOC analyte must be known and should be less than about 5 μg/L; (2) analysis was done by a laboratory certified by the U.S. Environmental Protection Agency; (3) the location of the well from which the sample was collected is known by latitude and longitude; (4) the sample was collected from untreated (raw) water; (5) the water sample was collected at or near the well head before being held in a pressure or holding tank; (6) the VOC analyte name is identified by parameter code (P code), and the analyte concentration is known; (7) the date (at a minimum, the year) of sample collection is known; and (8) quality-control data have been used to evaluate and, if necessary, to censor and(or) codify the environmental data prior to its compilation at a national level, to the extent that quality-control data are available. Characteristics of each monitoring program (Lapham and Tadayon, 1996, supplemental information) also were recorded as part of an inventory prior to program selection and compilation of VOC data. In addition to the information above, supporting, ancillary data also were requested for each VOC analysis, if readily available in electronic format (Lapham and Tadayon, 1996, table 3). The focus of this article is on the supporting, ancillary data.

VOC data from 47 nonpoint-source monitoring programs in the conterminous U.S. (Figure 1) currently (1999) are included in the retrospective data set, although compilation of additional data is an ongoing effort. Characteristics of each program are provided in Lapham et al. (1997, Table 5). Characteristics of all 47 monitoring programs combined are summarized in Table 1. Wells from each of the 47 programs were selected to develop unbiased, random, equal-area distributions of sampling sites (well networks) throughout all or parts of the aquifers sampled in these programs. The two most common

Figure 1. Approximate locations of the centers of the 47 monitoring programs or networks from which VOC data have been compiled into the retrospective data set (as of May 1999).

Table 1. Characteristics of the Ground-Water VOC Retrospective Data Set (August, 1998)

[VOC: volatile organic compound]

General information	
Number of monitoring programs	47
Number of States included	21
Number of wells	5,320
Sampling period	1985-1995
VOC analyses	
Range of the number of VOCs analyzed per sample	24 to 50
Range of reporting levels, in micrograms per liter	0.1 to 10 [1]
Percentage of analyses within indicated ranges of reporting levels (micrograms per liter):	
≤ 0.2	27
> 0.2 to ≤ 0.5	44
> 0.5 to ≤ 1.0	14
> 1.0 to ≤ 5.0	14
> 5.0 to ≤ 10.0	< 1
Well characteristics	
Range in depth of well below land surface, in feet	4 to 3,290
Median depth of wells below land surface, in feet	171
Percentage of wells screened in unconsolidated aquifers	54
Percentage of wells screened in or open to consolidated aquifers	38
Percentage of wells for which the above information was not recorded	8
Use of water from the well:	
Percentage of wells used for public supply	37
Percentage of wells used for domestic supply	15
Percentage of wells that are unused (i.e., an observation well)	9
Percentage of wells used for irrigation	5
Percentage of wells used for industrial purposes	0.6
Percentage of wells used for commercial purposes	0.4
Percentage of wells used for purposes other than those above	3
Percentage of wells that do not have "use of water" recorded	30

[1] Analyses that had a reporting level greater than 10 micrograms per liter were excluded from this data set because they are believed to have been diluted prior to analysis.

objectives of the 47 programs were to monitor ground water at the local, State, or aquifer scale, or to monitor the quality of drinking water from supply wells at the well head.

Purpose and Scope

The purposes of this article are to: (1) summarize 11 attributes of the ground-water VOC retrospective data set (the VOC analyte list and the associated reporting levels for each VOC, well type, well-casing material, type of openings in the interval(s), well depth, depth to the top and bottom of the open interval(s), depth to the water level in the well, aquifer type and aquifer lithology); (2) discuss and demonstrate the importance of these attributes for a national assessment of the occurrence of VOCs in ground water; and (3) suggest enhancements of VOC-sampling programs that would improve our understanding of VOC occurrence in ground water at regional and national scales. The scope of this assessment is focused on aquifers, or those parts of aquifers, that are currently used or have the potential to be used as sources of water supply for any use, but particularly for use as a source of drinking water.

SUITABILITY AND ENHANCEMENTS OF THE RETROSPECTIVE DATA SET

Approach Used by NAWQA to Answer Occurrence Questions

Sound natural-resource management decisions require information about both the presence and absence of contaminants of interest, and explanation of occurrence patterns when particular contaminants are detected frequently or at high concentrations in ambient ground water. The NAWQA Program seeks to answer a range of occurrence questions that ultimately might serve as the basis for technically sound, natural-resource management decisions.

There is a wide range in the complexity of questions related to VOC occurrence (Lapham et al., 1997). For example, one of the simplest, yet important occurrence questions is, "What percentage of the sampled wells contain a regulated VOC at a concentration that exceeds its Maximum Contaminant Level (MCL) under the Safe Drinking Water Act?" Answering this occurrence question is relatively simple and only requires knowledge of the number of wells sampled, the number of wells that had one or more VOCs detected above MCLs, and the laboratory's reporting level. In contrast, answering other occurrence questions is considerably more complex and requires additional information. An example of such a question is "Are VOCs found in the deeper parts of unconfined aquifers or are they only present in the upper, more vulnerable portions of these aquifers?" Answering this question requires knowledge of the location of sampled wells, whether the aquifer in which each well is located is unconfined or confined, and information about the depth in the aquifer from which water is being withdrawn. This additional information, as well as other information about well construction and aquifer characteristics, is essential to answer a variety of complex, and sometimes unanticipated, occurrence questions. Unfortunately, previous monitoring efforts have not always incorporated ancillary data into computer databases. An important effort of the NAWQA Program is to fully populate ancillary data for each well sampled by NAWQA to provide information needed to answer these types of complex occurrence questions.

In addition to the need for ancillary data, answering occurrence questions about VOCs in ambient ground water requires large well networks and sub-microgram per liter reporting levels. These attributes are needed because VOCs are often reported as nondetected (i.e., below today's analytical detection capability), and when detected, the concentrations are typically low, at sub-microgram-per-liter levels. Establishing statistical relations among VOC occurrence and explanatory variables requires that "detections" be measured in a large number of wells. For example, even with detection limits of about 0.2 ug/L, only about 14 percent of the wells that have been sampled by NAWQA in rural areas have had detections of one or more VOCs (Squillace and others, written commun. 1999). The relatively low detection frequency requires that many wells be sampled to achieve a large number of wells in which VOC detections are recorded. Data from a network of 5,000 to 10,000 wells or more, if possible, is sought because of varied hydrogeologic settings, aquifer types, land-use practices, and chemical-release patterns across the U.S. Resources available within the NAWQA Program today (1999) allow the sampling of about 2,500 wells per 10-year cycle for broad-scale occurrence assessment. Therefore, as noted previously, sampling by the NAWQA Program needs to be augmented with results of sampling from comparable monitoring networks operated by State and other agencies.

The NAWQA Program has lower detection levels for the analysis of VOCs in ambient ground water than those in many other monitoring programs. For about the last 10 years, the USGS has analyzed VOC samples at the USGS National Water-Quality Laboratory (NWQL) using purge and trap capillary gas chromatography/mass spectrometry (Rose and Schroeder, 1995) that has a reporting level for most VOCs of 0.2 micrograms per liter (µg/L). This reporting level was decreased even further in 1997, and most VOCs are now detectable at concentrations of 0.05 µg/L or less (Connor et al., 1998). Such low reporting levels are possible partly because of the generally lower concentrations that are associated with non-point sources of contamination in contrast, for example, to ground water at a point-source release, such as a gasoline-spill.

The benefit of having low analytical reporting levels for assessment of the occurrence of VOCs in ambient ground water is illustrated in Figure 2. This figure was developed from VOC analyses of water samples from wells near the water table beneath urban areas (urban land-use studies), collected between 1993-95 by the NAWQA Program (Squillace et al., 1996). All analyses were completed at the USGS NWQL at a reporting level of 0.2 µg/L. Figure 2 was constructed by artificially censoring the data set at 12 different reporting levels ranging from 0.2 to 10 µg/L, and calculating the percentage of wells that would have been recorded as having a detection of one or more VOCs at each of these 12 reporting levels. Figure 2 indicates that the percentage of wells in which one or more VOCs were detected at various reporting levels does not increase notably as the reporting level decreases from 10 µg/L to about 2.0 µg/L. However, a notable increase in the percentage of wells in which one or more VOCs were detected occurs as the reporting level decreases from 2.0 µg/L to 0.2 µg/L. The percentage of urban wells in which one or more VOCs were detected at a reporting level of 2.0 µg/L is about 22 percent, but increases to about 54 percent at a reporting level of 0.2 µg/L.

One objective of the NAWQA VOC National Synthesis is to try to determine the primary natural and human factors that relate or do not relate to VOC occurrence at national, regional, and aquifer scales. Moran and Davis (1998) determined that, at a national scale, the probability of an occurrence of any of 5 VOCs in ground water was

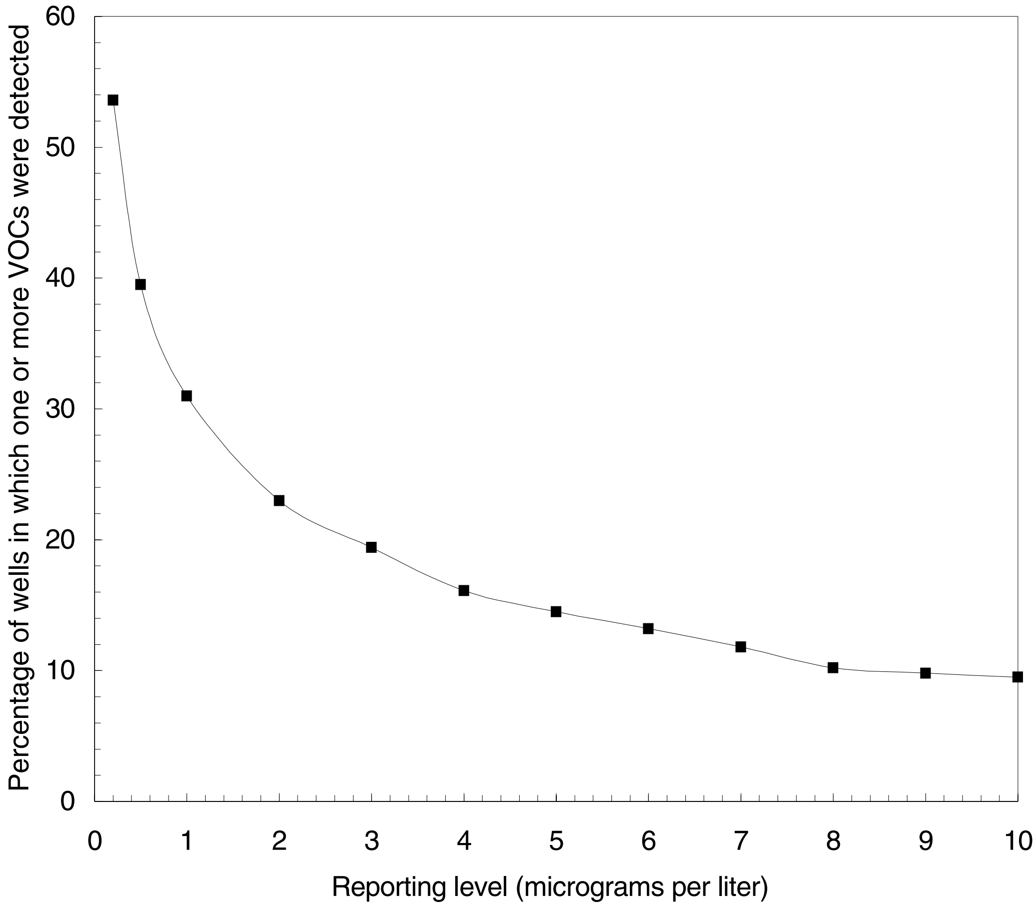

Figure 2. Relation between the percentage of urban land-use study wells sampled by the National Water-Quality Assessment Program in which one or more volatile organic compounds (VOCs) were detected and the reporting level.

related to use of the well and use of water from the well (e.g. well type), confining conditions of the aquifer, and land use in an 800 meter radius around the well. Several local NAWQA studies also have determined that VOC occurrence is related to both natural and human factors, and that the relational factors also can depend on the VOC being studied. For example, Andrews et al. (1995) reported that VOCs generally were detected at similar frequencies but at greater concentrations in water samples from wells completed in sand and gravel aquifers than in water samples from wells completed in bedrock aquifers in parts of the upper Mississippi River Basin. Grady (1997) reported that in southern New England the overall frequency of VOC detections was not significantly different for surfical and bedrock aquifers, but that the types of compounds detected in the two aquifers differed - 25 compounds were present in water samples from the surficial aquifers, but only four of these compounds were detected in water samples from bedrock wells. Grady (1997) also reported that: (1) VOCs were detected most frequently in monitoring wells from urban areas in comparison to undeveloped and agricultural areas; (2) that the fuel oxygenate methyl tert-butyl ether (MTBE) was more frequently detected in water samples from monitoring wells completed in ambient ground water located within a 0.25-mile of gasoline stations than elsewhere; and (3) the presence of VOCs in ground water does not appear to be directly related to the depth of wells.

Whereas Grady (1997) did not find a relation between the occurrence of VOCs and depth of wells in southern New England, this relation needs to be verified in other areas of the nation where geohydrologic conditions differ from those in southern New England. In addition, a relation between increasing well depth and decreasing concentrations of other water-quality constituents has been reported in other studies - for example, Mueller and Helsel (1996) observed this relation for nitrate. The decrease in nitrate concentration with depth was, in part, attributed to hydrogeologic conditions, such as the confined or unconfined nature of the aquifer studied. A relation between pesticide leaching and depth to the water table also has been reported (Domagalski and Dubrovsky,1992), and research into the occurrence of pesticides has shown that "younger" ground water is more likely to contain pesticides at detectable concentrations than "older" ground water (Kolpin and others, 1995; Domagalski and Dubrovsky, 1992). It is also known that the material from which the sampled well is constructed can affect concentrations of VOCs in ground water. For example, PVC has been shown to sorb chlorinated and nitroaromatic organic compounds (Parker and others, 1990; Parker and Ranney, 1994). The use of PVC primer and PVC adhesives to join sections of well casing and screen also have been shown to leach VOCs to water (Sosebee and others, 1983).

In summary, having adequate information to answer complex, as well as simple, VOC occurrence questions is important to sound management of the ground-water resources of the U.S. Doing so requires a large well network, analysis of a large number of VOCs at low reporting levels, and ancillary data associated with each sample, including location, information on well construction and aquifer properties, and sample collection and laboratory analytical methods.

Analysis of Eleven Attributes of the Retrospective Data

Because only data from raw-water samples at the well head were used, and because the location of each well sampled, the sampling date, and the analytical method used for analysis were minimum data requirements, this information is known for all samples in the data set. Other data attributes related to each sample also were requested (Table 2). These attributes were requested because these are considered essential to answering complex occurrence questions, and(or) because they provide supporting information about each sample often helpful when either resolving questions about the quality of the data or assessing the suitability of the data for a particular analysis. As indicated in Table 2, these data attributes are documented in the data set to varying degrees.

Simple occurrence assessment only requires basic information about a sample, such as the VOC concentration, sampling date, and sample location. Answering more complex occurrence questions requires additional information related to each sample (for example, see Andrews et al. (1995), Domagalski and Dubrovsky,(1992), Grady (1997), Kolpin et al. (1995), Moran and Davis (1998), and Mueller and Helsel (1996)). Based on these and other studies, eleven additional attributes are considered by the authors to be key minimum information necessary to interpret and explain VOC occurrence in ground water. Of these 11 attributes, two are related to laboratory analysis of VOCs in each ground-water sample:

1. The VOC analyte list.

Table 2. Data associated with each VOC analysis needed for use in assessment of occurrence, status, and distribution of VOCs in ground water, to the extent available.

[These data were compiled for each sample to the extent available from easily accessible electronic databases; VOCs, volatile organic compounds]

Data Elements	Percent of Samples with Data Element Populated
Well-identifier information	
Site-identification number	100
Agency collecting, analyzing, or reporting the data	91
Location data	
Latitude	100[1]
Longitude	100[1]
State	100[2]
County	100[2]
Well site and construction data	
Type of site (e.g.: well, spring, etc)	100[3]
Altitude of land surface	67
Primary use of well (e.g: observation, test, withdrawal, etc)	69
Primary use of water (e.g: domestic supply, public supply, industrial supply, unused, etc.)	70
Well depth	74
Depth to water in the well	20
Well-casing material	25
Depth to the top of the open interval	40
Depth to the bottom of the open interval	39
Type of opening in the interval (e.g. open hole, wire-wound screen, slotted casing, etc.) (information on material type of screens was not requested).	38
Information about the aquifer sampled	
Name of aquifer sampled	67
Aquifer type (unconfined, confined)	14
Aquifer lithology	19
Depth to the top of the water-bearing zone sampled	17
Depth to the bottom of the water-bearing zone sampled	9
Sampling information	
Date of sampling	100[4]
Time of sampling	73
Sampler type (e.g.: submersible positive pressure pump, peristaltic pump, bladder pump, etc.)	0.3
Sample purpose (e.g.: sample-related problem, irrigation effects, injection, seepage study, quality assurance, etc.)	15
Pump or flow period prior to sampling	13
Sample source (e.g.: well head, drill-stem testing, tap near well, multiple water wells, etc.)	100[5]
Sampling condition (e.g.: production and development test, injector site monitor, the site was being pumped, the site has recently been pumped, etc.)	14
Well-selection criteria (Site selected because it is near/within local problem area or site selected without regard to local problem area)	15
VOC-concentration data	See figure 3
Analytical reporting level for each analyte for each analysis	100[6]

[1]Location by latitude and longitude were required for a sample to be selected.
[2]State and county can be determined because the latitude and longitude are known.
[3]Only VOC data from wells were selected for inclusion in the data set.
[4]At a minimum, knowledge of the year of sampling was required for a sample to be selected.
[5]All samples selected were of raw water collected at the well head.
[6]Inferred from VOC-concentration data, as discussed in the text.

2. The reporting level associated with each analyte for each analysis.

And the remaining 9 attributes are related to the well sampled. The authors consider these 9 attributes to be the minimum information that should be known and recorded in a database about a sampled well:

3. Type of well sampled (primary use of water from the well).
4. Well-casing material.
5. The type of openings in the interval (open hole, wire-wound screen, etc.) and openings material type, if the opening is screened.
6. Well depth.
7. Depth to the top of the open interval(s).
8. Depth to the bottom of the open interval(s).
9. Depth from land surface to the water level in the well.
10. Aquifer type (confined, unconfined).
11. Lithology of the aquifer contributing water to the well.

Analysis of these eleven attributes in the retrospective data set provides insight into the retrospective data set's suitability to augment NAWQA data for interpretation and explanation of VOC occurrence in ground water, as discussed in the following sections.

VOC Analyte List

NAWQA's VOC analyte list contains a large number (55) of VOCs because documenting which VOCs are not detected in ground water is considered as important for a national occurrence assessment as is documenting which VOCs are detected. These 55 VOCs were selected using a three-step process: an initial selection and preliminary screening of 130 candidate compounds on the basis of available information; laboratory studies to ascertain the feasibility of analysis by purge-and-trap gas chromatography / mass spectrometry; and analysis of ground-water, surface-water, and quality-control samples to ascertain the performance of laboratory methods on environmental samples (Bender et al., 1999). Fifty-three of these 55 VOCs were compiled into the retrospective data set (1,3-dichlorobenzene was inadvertently omitted from the list of requested analytes; 1,3- and 1,4-dimethylbenzene are reported together). A frequency of analysis of the 53 VOCs indicate that State and local monitoring programs seldom analyze for the large number of VOCs analyzed by NAWQA. However, more than one-half of the 53 compounds were analyzed for in at least one-half of the samples, and 9 compounds were analyzed for in at least 90 percent of the samples (Figure 3). 1,1,1-Trichloroethane, tetrachloromethane, and trichloromethane were the three most frequently analyzed compounds (Figure 3). The VOCs in Figure 3 are organized by predominate use in the U.S. Many of these compounds, however, have other uses as well. Twelve of the 13 most frequently analyzed VOCs are in the use category of solvents, industrial reagents, and refrigerants. Other compounds of current interest were not frequently analyzed for. MTBE, a gasoline oxygenate, was analyzed for in only about 6 percent of the samples. Three other gasoline oxygenates (diisopropyl ether, ethyl tertiary-butyl ether, and tertiary-amyl methyl ether) and bromoethene were not included in any of the analyses in the data set.

Only about 37 percent of the wells in the data set are used for public drinking-water supply (Table 1). Nevertheless, the frequency of analysis of an individual VOC between 1985-95 generally seems to be closely associated with the regulatory history of that VOC, as illustrated in Figure 4 using four example compounds. Chlorodibromomethane is one of four trihalomethanes that began to be regulated in drinking water in 1979 (U.S. Environmental Protection Agency, 1979). This VOC was analyzed for in nearly all samples in the data set between 1985-95. Trichloroethene began to be regulated in 1987 (U.S. Environmental Protection Agency, 1987) and also was analyzed for in nearly all samples in the data set between 1985-95. 1, 2 Dichlorobenzene began to be regulated in 1991 (U.S. Environmental Protection Agency, 1991). The frequency of analysis of this compound was relatively low from 1985 through about 1987. Since 1987, the frequency-of-analysis of this compound increased to include about 80 percent or more of the samples analyzed from 1989-95. MTBE was not regulated as of 1995, and was analyzed for in less than 20 percent of samples until about 1995 when the frequency of analysis for that compound increased to about 50 percent.

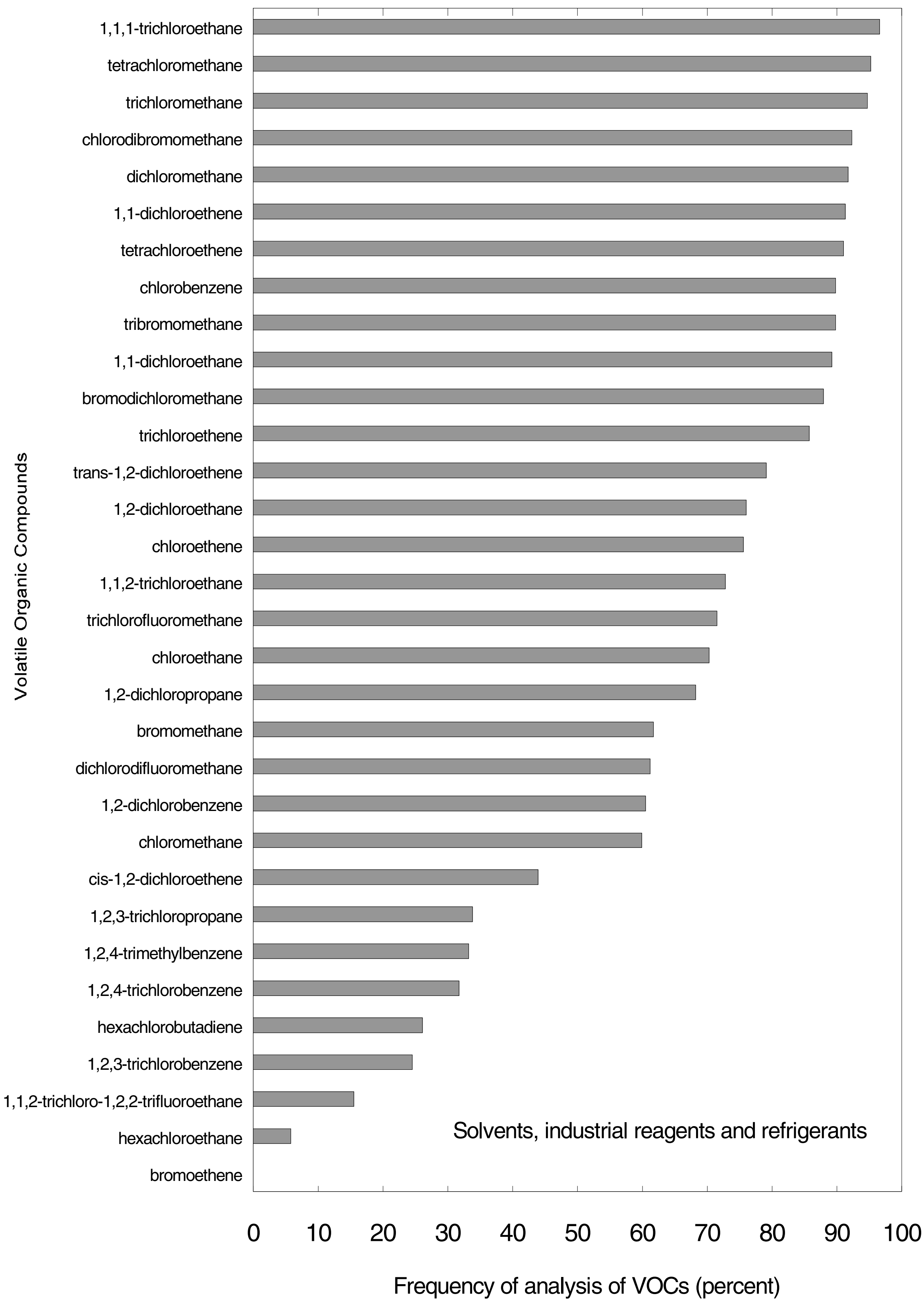

Figure 3. Frequency of analysis of 53 volatile organic compounds (VOCs) in the retrospective data set by predominant-use categories.

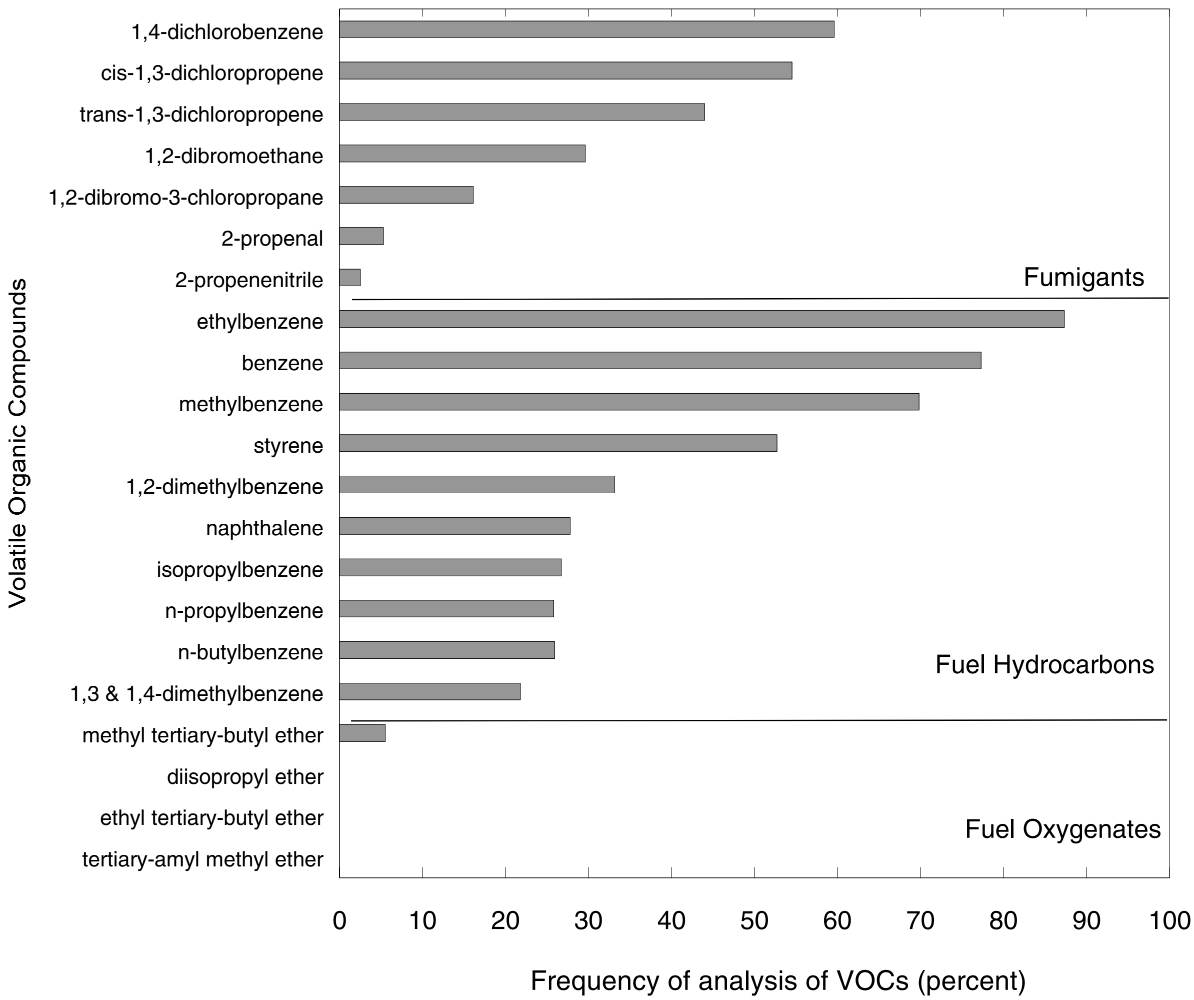

Figure 3 continued. Frequency of analysis of 53 volatile organic compounds (VOCs) in the retrospective data set by predominant-use categories (continued).

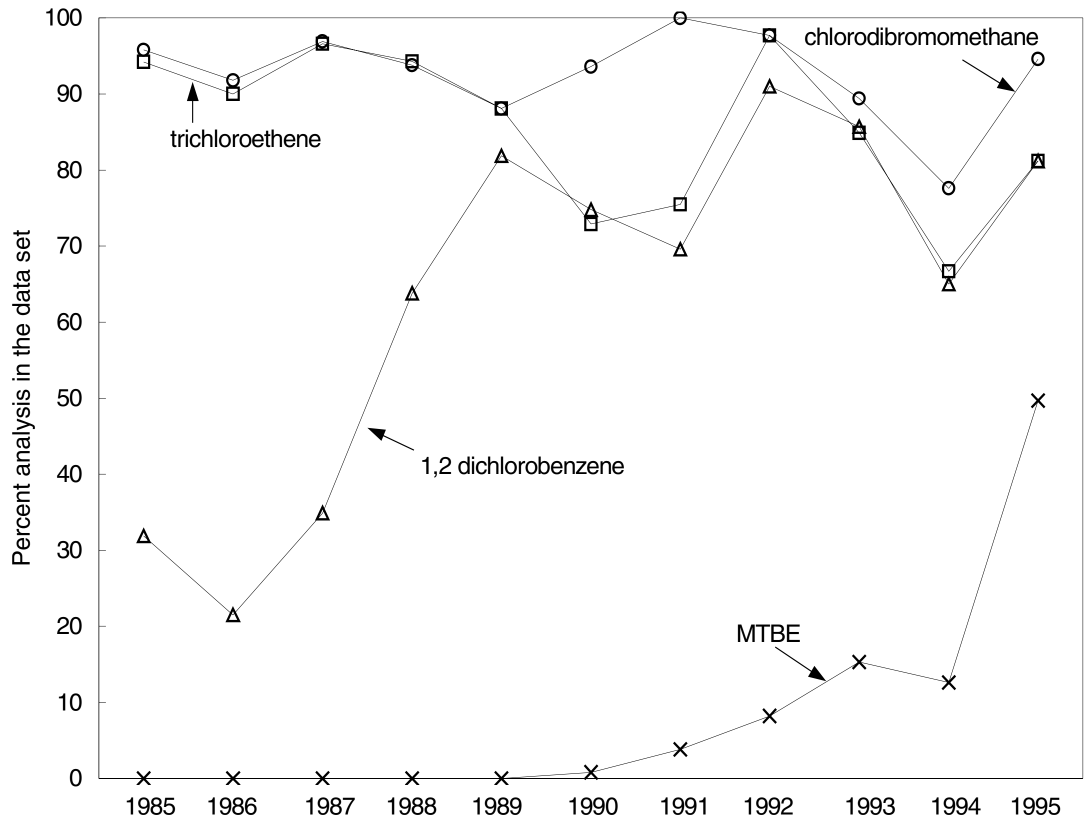

Figure 4. Frequency of analysis of four example volatile organic compounds (VOCs) in the retrospective data set from 1985 through 1995.

Reporting Levels

The two most common objectives of the 47 monitoring programs from which the VOC data were compiled were to monitor 'ambient' ground water at the local, State, or aquifer scale, or to monitor the quality of drinking water from supply wells at the well head. Based on an inventory of the monitoring programs conducted prior to data compilation, most of the VOC analyses were done using purge-and-trap GC/MS USEPA methods. Some analyses also were done by the USGS National Water-Quality Laboratory using similar laboratory methods. 'Less-than' values reported in the data set were typically about an order of magnitude higher than values that would be expected if the Method Detection Limit (MDL) was used to report nondetections. Consequently, the authors concluded that reported 'less-than' values were not based on MDLs, but rather on other, probably variable, 'reporting levels' that are considerably higher than the MDL. For this reason, the term 'Reporting Level' is used in this article.

Assessment of VOC occurrence cannot be completed without knowledge of the reporting level for each analyte for every analysis, including the reporting level associated with a detection of a compound. The reason for this is that the level at which the assessment of occurrence is made (the assessment level) must be prescribed, and all data need to be censored to this prescribed assessment level before use in an occurrence calculation. If the reporting level for each analyte for every analysis is not known, it has to be inferred, or the analyte has to be deleted from the data set using a uniform decision process such as the one presented in Figure 5.

Knowledge of the reporting level for each analyte for every analysis is particularly important when data are compiled into one collective data set from many monitoring programs. Recording reporting levels is particularly important in this case because VOC analyses are done by different laboratories at varying reporting levels. As an example, the VOC retrospective data discussed in this article was compiled from 47 monitoring programs or networks in 21 States. Reporting levels associated with the analytical methods among these programs vary between about 0.1 to 10 µg/L (Table 1).

Often the reporting level associated with a nondetection of an analyte can be easily inferred because the nondetection is reported as an unknown concentration less than the

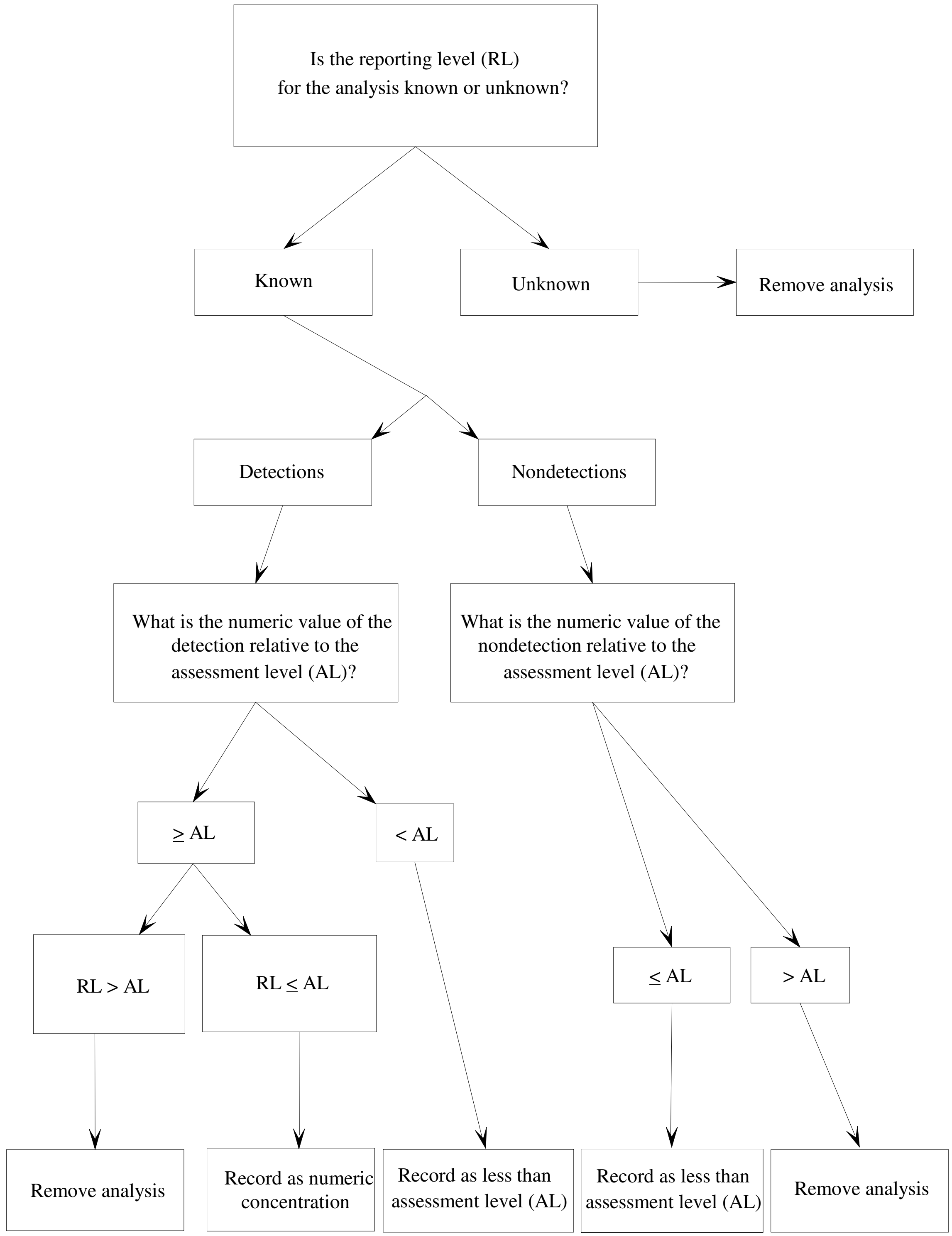

Figure 5. Decision diagram for censoring a data set that has multiple reporting levels to a prescribed assessment level for calculation of occurrence.

reporting level. The reporting level of the analytical method associated with a measured concentration of an analyte, however, usually is not recorded. Nevertheless, knowledge of that reporting level is required when censoring data to the prescribed assessment level prior to an occurrence calculation (Figure 5). The approach used here to determine an unrecorded reporting level was to infer it from reporting levels (e.g. less-than values) recorded for nondetections of the same VOC in samples collected from other wells in the same monitoring program during the same round of sampling. The validity of this approach to inferring unrecorded reporting levels for detections of VOCs is not known. Recording the reporting level of the analytical method associated with each measured concentration of a VOC in a water sample would be a valuable enhancement to data bases because it would eliminate the need for this type of inference.

Nearly all (99 percent) of the data in the retrospective data set were analyzed at a reporting level of 5 µg/L or less (Table 1). Consequently, most of the data can be used for an assessment of the occurrence of one or more VOCs at an assessment level of 5 µg/L or higher. However, only about 27 percent of the data were analyzed at a reporting level of 0.2 µg/L or less. Most NAWQA VOC data collected from 1993-95 were analyzed at a reporting level of 0.2 µg/L. Therefore, at most, only about 27 percent of the retrospective data are suitable to augment NAWQA data when addressing occurrence questions at the low assessment level of 0.2 µg/L.

Attributes of Each Well

As discussed previously, answering complex occurrence questions requires ancillary information about each sample and about each well sampled. In the view of the authors, nine attributes of each well sampled are minimum critical information for answering complex occurrence questions. These nine attributes are: (1) the type of well sampled; (2) the well-casing material; (3) the type of openings in the interval (open hole, wire-wound screen, etc.) and openings material type, if the opening is screened; (4) the well depth; (5) depth to the top of the open interval(s); (6) depth to the bottom of the open interval(s); (7) the depth from land surface to the water level in the well; (8) aquifer type (confined or unconfined) and (9) the lithology of the aquifer at the interval contributing water to the well. The degree to which these nine attributes and combinations of these attributes are populated in the retrospective data set for each well will partly determine the usefulness of the VOC analysis from each well in augmenting NAWQA data for occurrence assessment.

The percentage of wells that have each of the nine attributes populated in the retrospective data set is shown in Table 2. Seventy-four percent of the wells in the retrospective data set have information on well depth and 70 percent have information on well type, but only 14 percent of the wells have information about the type of aquifer contributing water to the well (Table 2). Consequently, about 74 and 70 percent the wells, respectively, are potentially suitable for use in investigating the relation between VOC occurrence and well depth or well type, but only 14 percent of the wells are potentially suitable for use in investigating the relation between VOC occurrence and aquifer type. The depth to water in the well, casing material, depths to the top and bottom of the open interval(s), the type of openings in the open interval(s), and aquifer lithology are all known in less than 50 percent of the wells.

Investigating many complex occurrence relations requires combinations of several attributes about a well. Only a small percentage of wells have many of these combinations of attributes documented in the data set (Figure 6). For example, only about 8 percent of the wells have information on the four attributes - well depth, well type, water level, and aquifer lithology. Consequently, only 8 percent or less of the wells are potentially suitable for multivariate analyses, such as principal-components analysis, of the relation between VOC occurrence and these four variables.

The percentages cited in the previous paragraph were calculated for each of the nine attributes or combinations of attributes regardless of reporting levels. If the assessment level selected for the occurrence assessment is low -- for example, 0.2 µg/L -- the percentage of wells with both the indicated attributes of the well populated and this low reporting level would likely be less than the percentages shown in Figure 6.

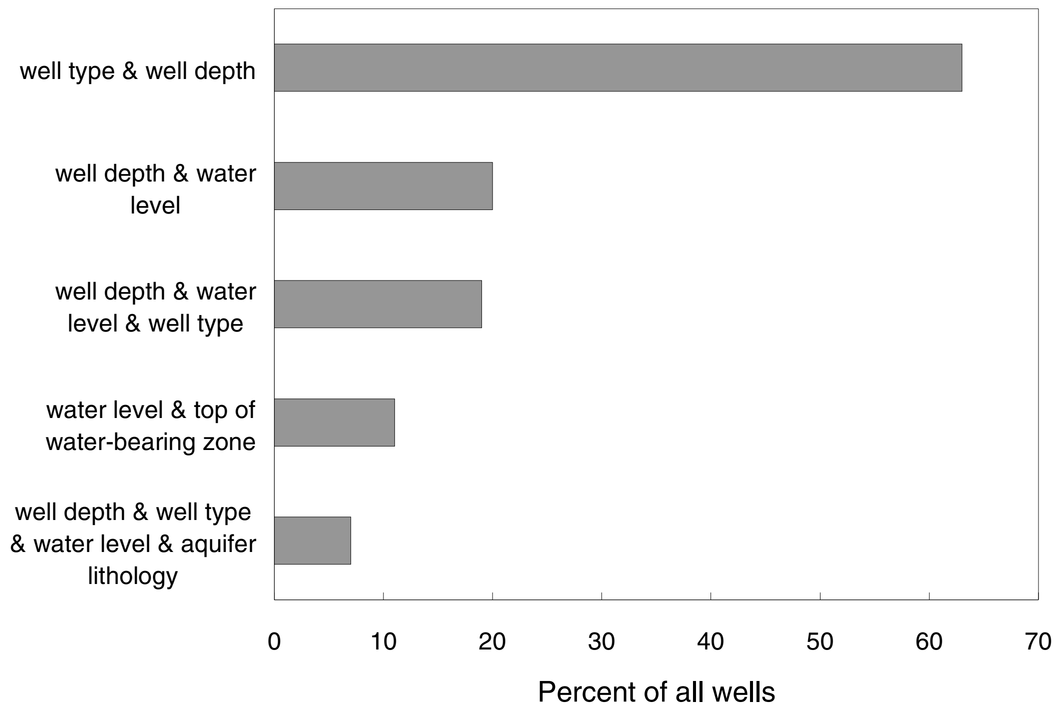

Figure 6. Percent of wells that have the indicated attribute or combination of attributes populated in the retrospective data set.

SUMMARY OF THE UTILITY OF THE RETROSPECTIVE DATA FOR OCCURRENCE ASSESSMENT AND SUGGESTED ENHANCEMENTS

The utility of the retrospective data for occurrence assessment depends on the question being asked. The utility of the data generally decreases as the complexity of the question increases, where complexity is measured by the information required to answer the question posed. For example, information that would be required to answer a relatively simple question about the occurrence of one or more VOCs in ground water of the U.S. would include the concentration(s) of the VOC(s) of concern and the laboratory reporting levels associated with each VOC in each water sample. More complex questions also might require locational information and various combinations of ancillary information, such as the depth of each well sampled, the depth from land surface to the water level in each well, well type, well-casing material, type of openings and material types for well screens, the depths to the top and bottom of the open interval(s), and the type and lithology of the aquifer contributing water to each well.

Analysis of the characteristics of the retrospective data described in this article indicates that the three greatest limitations of using retrospective data for addressing national and regional occurrence questions are inadequate: (1) numbers of VOC(s) of interest included in the analysis; (2) information on the reporting level for each VOC analyzed; and (3) ancillary information about each sampled well. Although reporting levels were inferred for unrecorded reporting levels in the data set as discussed in this article, the validity of the approach used is not known. Therefore, the three most important enhancements to VOC data collected in Federal, State, and local nonpoint-source monitoring programs for use in a national assessment of VOC occurrence in drinking water would be an expanded VOC analyte list, recording the reporting level for each analyte for every analysis, and recording key ancillary information about each well.

In addition to the limitations just cited, another possible limiting feature of the retrospective data for use in augmenting NAWQA data is the relatively high laboratory reporting levels used by many laboratories for analyses of VOCs in water samples, as compared to the reporting level commonly used by NAWQA. For occurrence assessment at 0.2 μg/L commonly used by NAWQA, only a small percentage of the retrospective data is suitable to augment NAWQA data, even at the national scale. However, further analysis would be useful in evaluating the relative benefit of lower reporting levels (0.2 μg/L versus 10 μg/L, for example) in explaining the occurrence of VOCs in ground water.

BENEFITS OF ENHANCEMENTS

Enhancing nonpoint-source ground-water monitoring programs for VOCs would enable the data to be used collectively to answer a range of simple to complex questions about the occurrence of VOCs in ground water at national and regional scales. Enhancements, such as measuring a larger number of VOCs at a reporting level that is less than often used today and recording characteristics about each well and aquifer sampled, would:

1. Result in a more complete assessment of the occurrence of VOCs in ground water nationwide by documenting the absence as well as the presence of VOCs at a low reporting level.
2. Explain possible reasons for occurrence and nonoccurrence.
3. Provide data in support of the Safe Drinking Water Act on the occurrence of currently unregulated VOCs that might be regulated in the future.
4. Provide VOC data that might be needed in the future to address unanticipated questions of regional or national concern as they arise, for example provide an early warning of the occurrence of a VOC in ground water resources used for drinking water.

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