Health Consultation

Lakeland Groundwater Contamination Plume

City of Lakeland, Washington County, Minnesota

MPCA Site Response Number SR145

January 24, 2001

Prepared By:

The Minnesota Department of Health
in Cooperative Agreement with the
Agency for Toxic Substances and Disease Registry

FOREWORD

This document summarizes potential public health concerns associated with a plume of contaminated groundwater in Afton, Lakeland, and Lakeland Shores, Minnesota. The plume may be associated with Tower Asphalt, Inc. (Tower). This document is based on a formal site evaluation prepared by the Minnesota Department of Health (MDH). A number of steps are necessary to do such an evaluation, and include the following:

Evaluating exposure: MDH scientists begin by reviewing available information about environmental conditions at the site. The first task is to find out how much contamination is present, where it is found on the site, and how people might be exposed to it. Usually, MDH does not collect its own environmental sampling data. We rely on information provided by the Minnesota Pollution Control Agency (MPCA), U.S. Environmental Protection Agency (EPA), and other government agencies, businesses, or the general public.

Evaluating health effects: If there is evidence that people are being exposed—or could be exposed—to hazardous substances, MDH scientists will take steps to determine whether that exposure could be harmful to human health. The report focuses on public health—the health impact on the community as a whole—and is based on existing scientific information.

Developing recommendations: In the evaluation report, MDH outlines its conclusions regarding any potential health threat posed by a site and offers recommendations for reducing or eliminating human exposure to contaminants. The role of MDH in dealing with hazardous waste sites is primarily advisory. For that reason, the evaluation report will typically recommend actions to be taken by other agencies—including EPA and MPCA. However, if there is an immediate health threat, MDH will issue a public health advisory, warning people of the danger, and will work to resolve the problem.

Soliciting community input: The evaluation process is interactive and ongoing. Typically, MDH begins by soliciting and evaluating information from various government agencies, the organizations responsible for cleaning up the site, and the community surrounding the site. Any conclusions about the site are shared with the groups and organizations that provided the information. Once an evaluation report has been prepared, MDH seeks feedback from the public. *If you have questions or comments about this report, we encourage you to contact us*.

Please write to: Community Relations Coordinator
Site Assessment and Consultation Unit
Minnesota Department of Health
625 Robert St. N., Box 64975
St. Paul, MN 55164-0975

OR call us at: (651) 201-4897 or 1-800-657-3908
(toll free call—press "4" on your touch tone phone)

Statement of Issues

A contaminated groundwater plume, which may have originated at Tower Asphalt, Afton Minnesota, contaminated private wells in Lakeland and Lakeland Shores, Minnesota, in the late 1980s (MPCA 1996). There is no legal link between Tower and the Lakeland groundwater contamination plume. A municipal water system was installed in Lakeland in the early 1990s. However, residents were financially responsible for any hookups if the contamination concentration in their well was below the well advisory level specified in the Record of Decision for the site. Therefore, some residents are not connected to the municipal water system and continue to use well water.

Due to the low level of contamination, the belief that contamination levels are decreasing, and the availability of a clean water alternative for most of the residents, the Minnesota Pollution Control Agency (MPCA) has proposed removing the Lakeland site from its Site Response listings. MPCA requested that MDH provide comments on this proposal. Delisting would include discontinuing the sampling of private drinking water wells in the cities of Lakeland and Lakeland Shores. This health consultation is based on MDH review of the following site information:

- July 1995 report titled *Remedial Investigation Report, Tower Asphalt, Inc., Lakeland, Minnesota*, prepared by Dames & Moore, Inc. (RI), excluding appendices (Dames & Moore 1995)
- May 1996 report titled *Remedial Investigation Corrective Action Design, Tower Asphalt, Lakeland, Minnesota*, prepared by Geraghty & Miller, Inc. (RI/CAD). excluding appendices (Geraghty & Miller 1996)
- Record of Decision, issued by the Minnesota Pollution Control Agency, April 2 1991 (ROD)
- Stipulation of Settlement, issued by the Minnesota Pollution Control Agency, May 28, 1996 (MPCA 1996)
- Results of recent private well sampling events conducted by MPCA
- Information regarding Lakeland and Lakeland Shores households that are hooked up to municipal water provided by the City of Lakeland
- Information regarding current Lakeland addresses provided by the City of Lakeland
- Information regarding current Lakeland Shores addresses proved by the City of Lakeland Shores

Information gathered as a result of this review was evaluated with the assistance of geographic information system (GIS) software. Melinda Salisbury and Carl Herbrandson, MDH, conducted a site visit on May 27, 1998.

Site Background

Tower Asphalt, Inc. (Tower) operated a bituminous batch plant west-northwest of the City of Lakeland, Minnesota, as illustrated in Figure 1. The site location is the SE 1/4 of Section 33, Township 29 North, Range 20 West. The site is hydrologically upgradient of Lakeland.

In addition to operating an asphalt plant, Tower leased a portion of the site to Steve's Oil Services (Steve's Oil). In July 1978, Steve's Oil documented a release of approximately 3,000 gallons of aviation fuel and a chlorinated solvent. A portion of the released fuel and solvent was recovered, and contaminated soil was removed and disposed of under MPCA review. Site monitoring wells, both on and downgradient of the site, as well as private drinking water wells in Lakeland, show evidence of contamination that is consistent with the released fuel and solvent.

The Remedial Investigation/Corrective Action Design identifies five volatile organic compounds (VOCs) as being the chemicals of concern (COCs) for the site. These COCs were specified because they were detected more often that other compounds. The five COCs identified in the RI/CAD are the following:

- 1,1, Dichloroethane (1,1-DCA)
- cis-1,2-Dichloroethene (c-1,2-DCE)
- Tetrachloroethene (PCE)
- 1,1,1-Trichloroethane (1,1,1-TCA)
- Trichloroethene (TCE)

In addition to these five VOCs, MDH is also concerned about the potential for vinyl chloride contamination in the identified plume.

Furthermore, nitrate is a potential concern in Lakeland and Lakeland Shores. The presence of nitrate is unrelated to the presence of the other COCs. Nitrate contamination is a common but potentially serious problem in Minnesota. Typically the nitrate contamination comes from the proximity of residential wells to septic drainfields or sources of animal waste.

Lakeland now has a municipal water supply that is available to most residents. However, a number of households continue to use private wells for drinking water, as illustrated in Figure 2.

Health Concerns

MDH has determined Health Risk Limits (HRLs) for the chemicals found in groundwater. For chemicals that are not carcinogens, consumption of water at concentrations at or below the HRL is considered to be safe, even if the water is consumed every day. Exposures to non-carcinogens

with similar endpoints are considered together to better represent the actual health risk to exposed individuals. A health hazard index was calculated by the consultants for Steve's Oil for these non-carcinogenic chemicals (Dames & Moore, 1995). The health hazard index was calculated by adding the fractions of the HRL that are found in the contaminated groundwater.

HRLs for carcinogens are concentrations in drinking water that are associated with a negligible cancer risk, even if the water is consumed every day. MDH considers a cancer risk to be a negligible health risk if it is less than or equal to one additional case of cancer in 100,000 individuals exposed for a lifetime. If individuals are exposed to more than one carcinogen, cancer risks associated with those exposures may be added to determine the total cancer risk from all chemicals. Again, the cancer risk from chemicals in drinking water is considered to be negligible if the combined risk is less than 1 in 100,000.

While MDH is concerned about the exceedances of HRLs for the carcinogens reported, MDH believes that sampling for additional compounds may be critical in determining the seriousness of the potential health risk to residents using well water. Significant quantities of precursors to vinyl chloride have been found, both above the bluff in monitoring wells and in private wells in Lakeland. These compounds include PCE (tetrachloroethylene) and TCE (trichloroethylene), as well as reductive dechlorination product *cis* 1,2-DCE (dichloroethylene). Further dechlorination of these compounds can lead to the formation of vinyl chloride.

Conditions in the plume can be considered favorable for the formation of vinyl chloride if it is detected either in the monitoring wells or residential wells. The HRL for vinyl chloride is 0.2 Fg/L, which, because vinyl chloride is a carcinogen, is the concentration in drinking water that is associated with a negligible cancer risk if the water is consumed over a lifetime. Although the method detection limit for vinyl chloride has been close to 0.2 Fg/L for the past few sampling events, sample handling procedures have been shown to have a significant effect on the measured concentrations of volatile compounds (Soule et al., 1996). Specifically, holding times between collection and analysis must be short to minimize the loss of vinyl chloride.

Summary of Sampling Results and Data Gaps

There is a significant lack of geologic, hydrogeologic, and chemical information in and around Lakeland and Lakeland Shores. These data gaps exist primarily because no monitoring wells were installed in Lakeland or Lakeland Shores. Due to the absence of monitoring wells in and around Lakeland, there is no information available with which to delimit the horizontal and vertical extent of the plume with any certainty. Additionally, without monitoring wells, there is no water level information available with which to derive groundwater flow information.

Historical analytical data from wells tested in Lakeland have shown carcinogen chemical contamination in wells. People drinking water from these wells could incur an incremental cancer risk above the MDH negligible cancer risk criterion. These data, when entered into a database containing geographic and household address information, appear to outline some geographical aspects of the plume (see Figure 3), although the plume is not well delimited. The

VOC area of interest that was evaluated by MDH is defined as the area bounded by 2nd Street North, the Lakeland western city limit, 3rd Street South, and the St. Croix River. Wells sampled more recently than 1990 are shown in green on Figures 3 and 4. Figure 3 illustrates the Lakeland area of interest, and Figure 4 illustrates the Lakeland Shores area of interest.

All recent sampling results show carcinogen concentrations below HRLs, and thus would have associated cancer risks less than one in 100,000 for any individuals consuming the water. However, well samples from the 1980s at these residences indicate carcinogen concentrations exceeding HRLs.

There appear to be no houses in Afton on a line between Tower and the Lakeland plume area. MDH did not review any data for wells located between Lakeland and Tower and did not evaluate whether or not there are drinking water wells in use in any potential residential areas between Lakeland and Tower. Additionally, between 1977 and 1991, nitrates were detected in wells at concentrations exceeding the HRL of 10 mg/L. It appears that four residences are still using wells that had previous nitrate HRL exceedances. The area of the nitrate HRL exceedances is illustrated on Figure 5. However, nitrate contamination may have multiple sources and cannot be considered a single 'plume'. There may be other residences at risk in Lakeland and Lakeland Shores.

Children's Health Initiative

In accordance with the Agency for Toxic Substances and Disease Registry's Children's Health Initiative and MDH policy, we are concerned about toxic exposures that may affect children differently than adults and, as a result, may not be addressed in a typical health assessment. This Health Consultation discusses questions about the potential contamination of private wells in the City of Lakeland. Children may be exposed to a proportionally greater amount of any contamination due to their typically higher respiratory rate and their greater surface area to weight ratio. Both of these characteristics increase children's need for and ingestion of water, and create a greater absorption potential for children during a respiratory or dermal exposure. Furthermore, it is believed that children, given the development and growth of their bodies, are often more susceptible to chemical toxicity, including the potential development of cancer following exposure to cancer causing agents.

Health risk assessments have been developed by the EPA, MDH, and other governmental entities to determine realistic health-based exposure limits that can be expected to protect the population, including the most sensitive individuals. Children are often defined as the most sensitive individuals. The HRLs, developed by MDH, set limits on the concentration of certain contaminants that should not be exceeded in potable water. These limits are intended to be protective of the health of children exposed to concentrations up to the HRL.

The presence of nitrates is the biggest children's health issue. The consumption of nitrates is known to cause adverse health effects in sensitive individuals, especially young infants. Methemoglobinemia, or "Blue baby syndrome" is caused by nitrates and nitrites in drinking

water, leading to oxygen deprivation, possible brain damage, and sometimes death. Infants with diarrhea may be a higher risk from nitrate and nitrite contaminated water. The federal Maximum Contaminant Level (MCL) and the MDH HRL for nitrates is 10 mg/L, and it is considered to be protective of sensitive individuals, including infants.

Historically, the chemicals of concern in the Lakeland groundwater plume have been 1,1, Dichloroethane (1,1-DCA), cis-1,2-Dichloroethene (c-1,2-DCE), Tetrachloroethene (PCE), 1,1,1-Trichloroethane (1,1,1-TCA), Trichloroethene (TCE).

- PCE (tetrachloroethylene), TCE (trichloroethylene), *cis* 1,2-DCE (dichloroethylene), and vinyl chloride are of health concern due to their cancer causing potential. The HRLs for these compounds were developed to protect sensitive individuals, and as such, should be protective of children. It is the understanding of MDH that a specific health risk assessment for vinyl chloride in children is being developed by EPA; however, the specific risk assessment is unavailable and has not been reviewed by MDH.

- 1,1, Dichloroethane (1,1-DCA) and 1,1,1-Trichloroethane (1,1,1-TCA) are not considered to be carcinogens. The HRLs developed for these compounds are considered to be protective of sensitive individuals, including children.

Conclusions

It is premature to delist the Lakeland site at this time. The presence of *cis* 1,2-DCE demonstrates that the contaminants in the groundwater plume extending into Lakeland are undergoing reductive dechlorination. Vinyl chloride is a product of the dechlorination of TCE and PCE. In the last few years sampling and chemical analysis methodology for vinyl chloride has changed significantly, allowing for more sensitive and accurate measuring of this contaminant in groundwater plumes. Given the cancer potency of vinyl chloride, MDH believes that it is important to determine if there is any vinyl chloride in the plume.

Although there have been exceedances of the HRLs in Lakeland, the private well sampling conducted during the 1990s does not indicate any exposures of public health concern. However, there is a lack of information regarding the horizontal and vertical extent of the plume.

Homes that are in and near this area that also use private wells may also be at risk for having nitrate-contaminated drinking water. Furthermore, because nitrate contamination may have multiple sources and cannot be considered a single 'plume', there may be other non-adjacent residences at risk in Lakeland and Lakeland Shores. Currently this site is categorized as posing "no apparent health hazard," but further data is needed to confirm this conclusion.

Recommendations

MDH recommends that the delisting of the Lakeland groundwater contamination plume be delayed until important data gaps can be addressed or residences that may have contaminated drinking water wells are connected to municipal water.

MDH recommends that all of the existing monitoring wells be tested for vinyl chloride and nitrates. MDH recommends that residential wells that may be reasonably expected to be contaminated with vinyl chloride or nitrates be sampled or resampled.

MDH recommends that proper sample collection and handling procedures are followed by analysis of the samples within 24 hours. The low level vinyl chloride detection methods and analysis, MDH 560, should be used for all samples. As shown in Soule, et. al (attached), up to 40% of the initial vinyl chloride concentration can be lost if samples are not analyzed within 24 hours.

Given the lack of current groundwater contamination data and the potential for well contamination from the historic Tower Asphalt plume or from nitrates, MDH recommends that residents in Lakeland and Lakeland Shores hook up to the municipal water system.

MDH recommends that if vinyl chloride is found in any residential or monitoring well that all residences in the vicinity of the plume in Lakeland and Lakeland Shores be connected to municipal water regardless of past contamination history.

MDH recommends that MDH and MPCA undertake further review of the site after receipt of VOC and vinyl chloride sampling results.

MDH also recommends that homeowners sample their private wells for nitrates annually.

Public Health Action Plan

MDH s Public Health Action Plan for the site consists of continued consultation with MPCA staff on the groundwater monitoring, and participation in any planned public outreach activities.

This consultation was prepared by:

Melinda Salisbury, P. E.
Hydrologist
and
Carl Herbrandson, Ph. D.
Toxicologist

Site Assessment and Consultation Unit
Environmental Surveillance and Assessment Section
Minnesota Department of Health

References

Dames & Moore, Inc. (1995) Remedial Investigation Report, Tower Asphalt, Inc., Lakeland, Minnesota. RI. Dames & Moore, Inc. 21819-003. New Brighton, MN. July 1995.

Geraghty & Miller, Inc. (1996) Remedial Investigation Corrective Action Design, Tower Asphalt, Lakeland, Minnesota. RI/CAD. Geraghty & Miller, Inc. Minneapolis, MN. May 1996.

Minnesota Pollution Control Agency. (1996) Stipulation of Settlement. Agreement. MPCA, State of Minnesota, St. Paul. Tower Asphalt, Inc. (5/23/96).

Minnesota Pollution Control Agency. (1991) Record of Decision, Lakeland Groundwater Contamination Site, Water Supply and Southern Plume Operable Units, Lakeland and Lakeland Shores, Washington County, Minnesota. (4/2/91).

ATTACHMENT 1

FIGURES

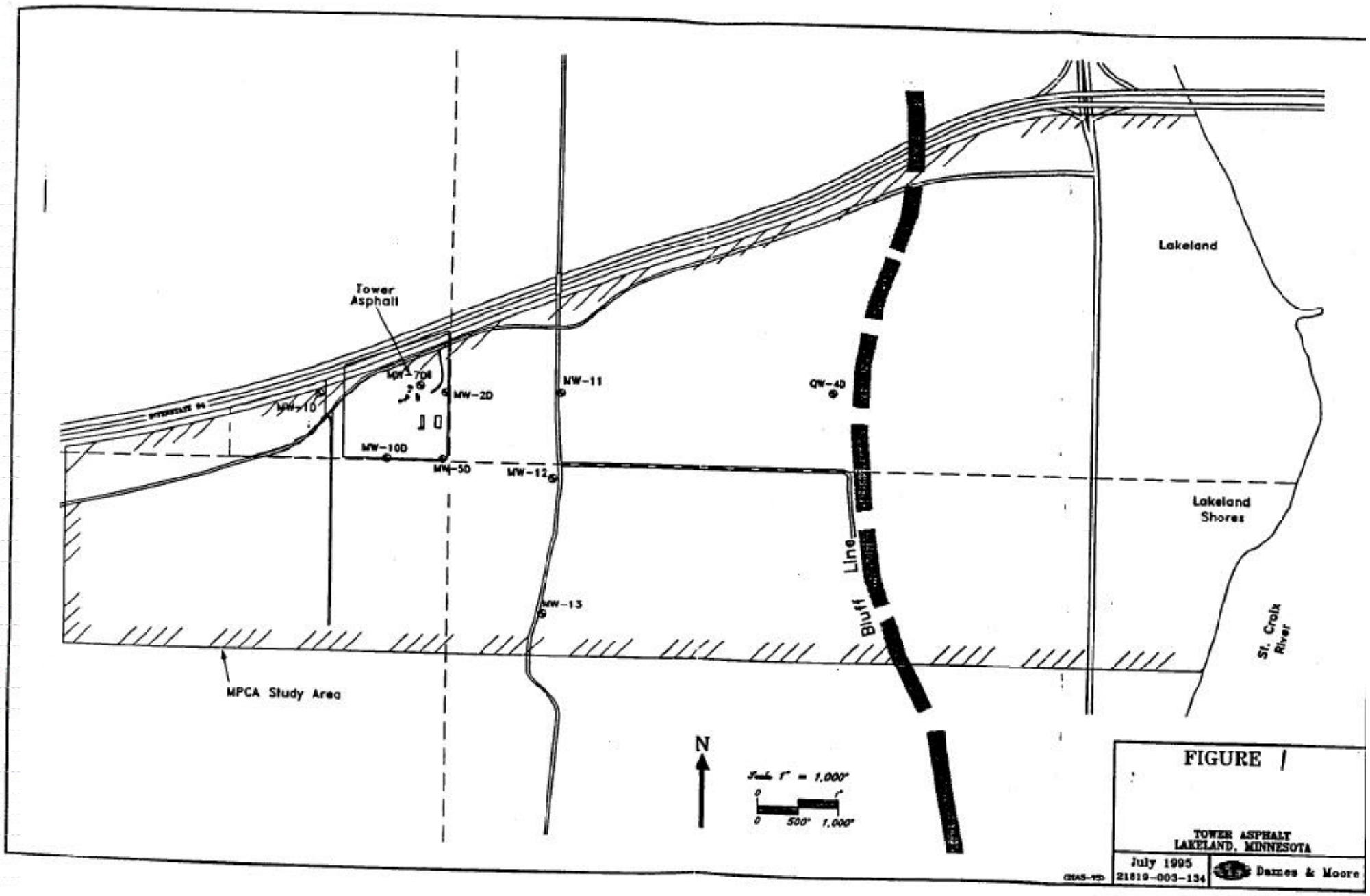


FIGURE 1

TOWER ASPHALT
LAKELAND, MINNESOTA

July 1995
21819-003-134

Dames & Moore

FIGURE 2
LAKELAND WATER HOOKUPS

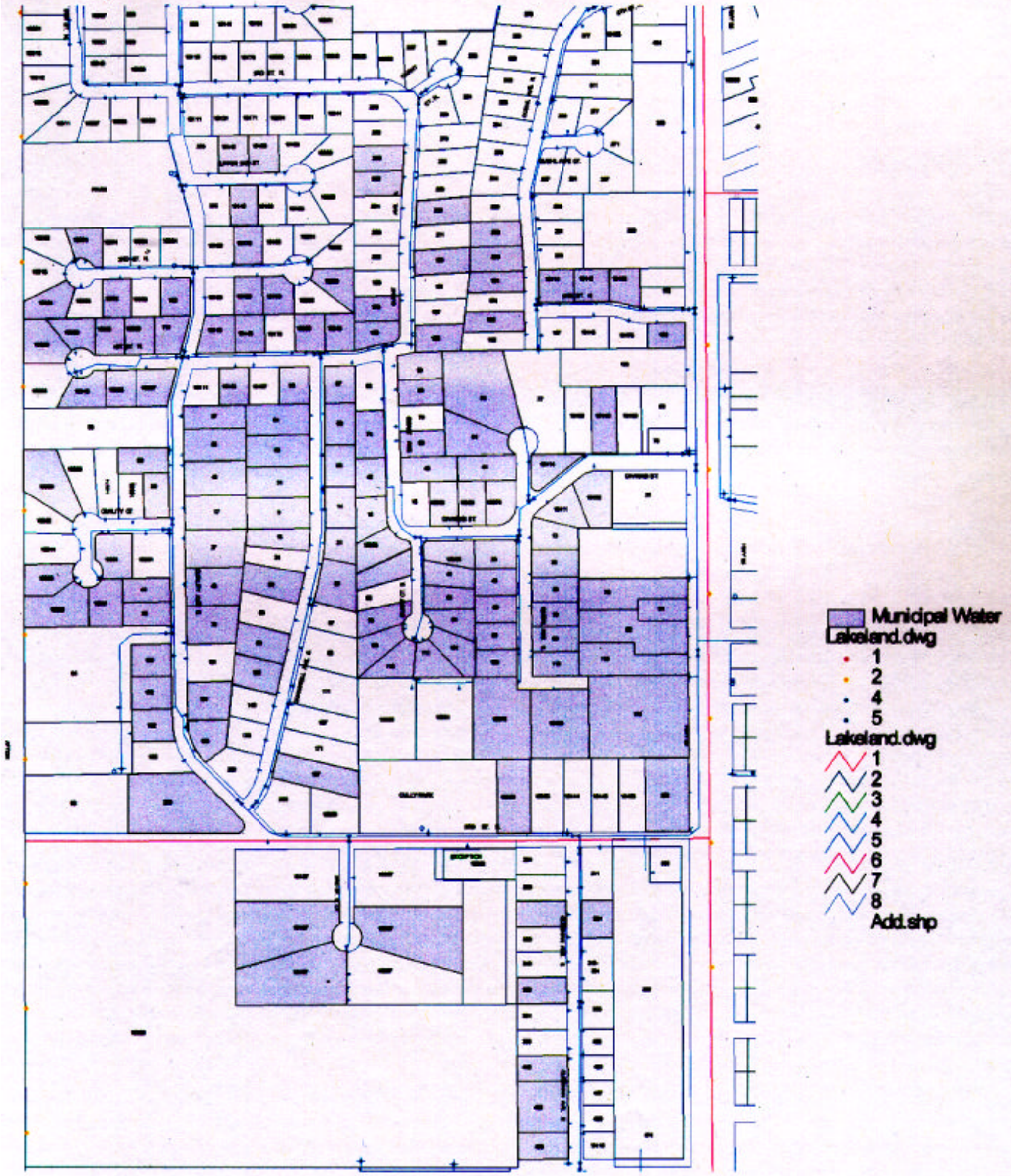
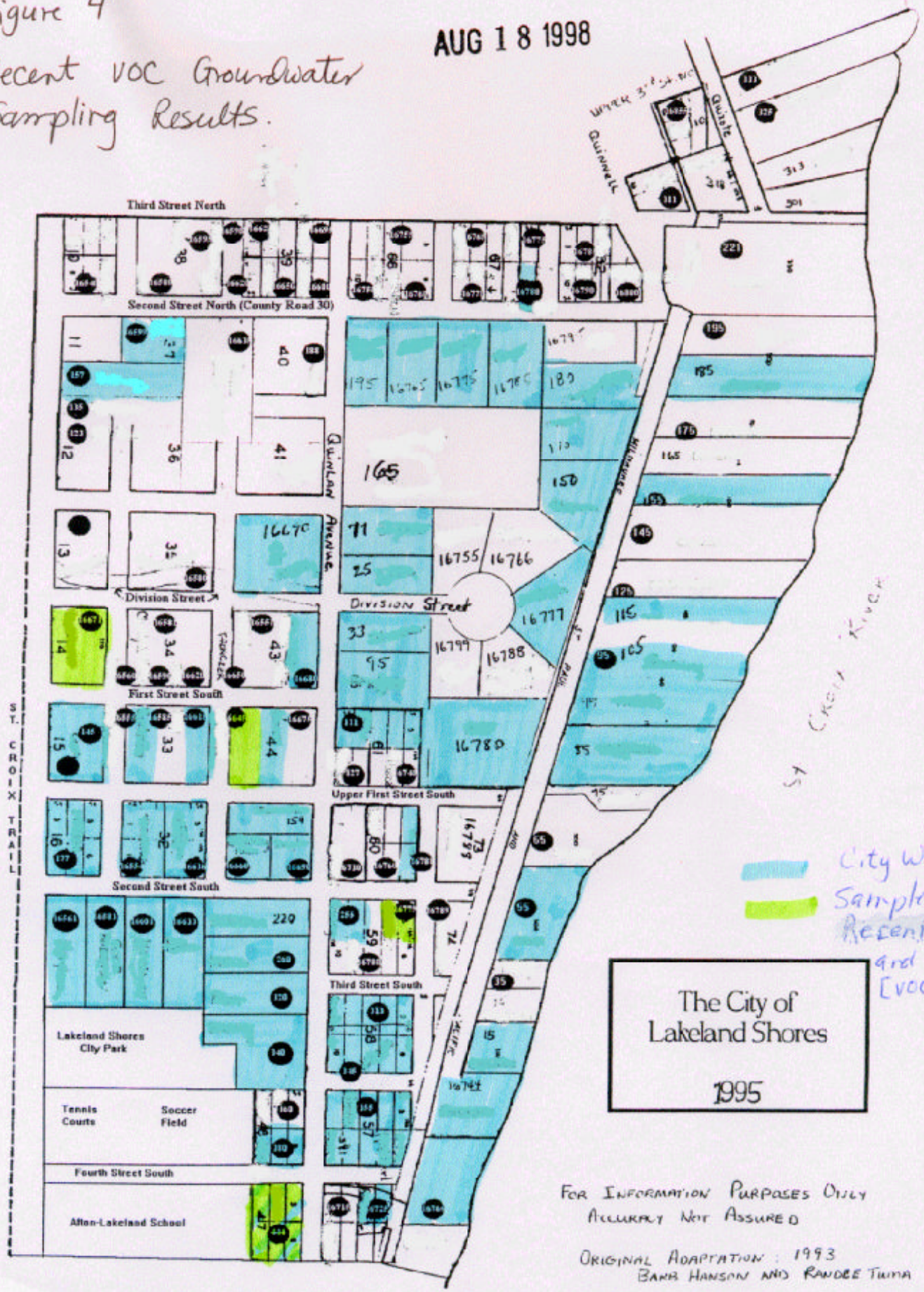


FIGURE 3 - LAKELAND, MN
SUMMARY OF PRIVATE WELL USAGE AND
PAST GROUNDWATER SAMPLING INFORMATION

Figure 4

Recent VOC Groundwater Sampling Results.

AUG 18 1998

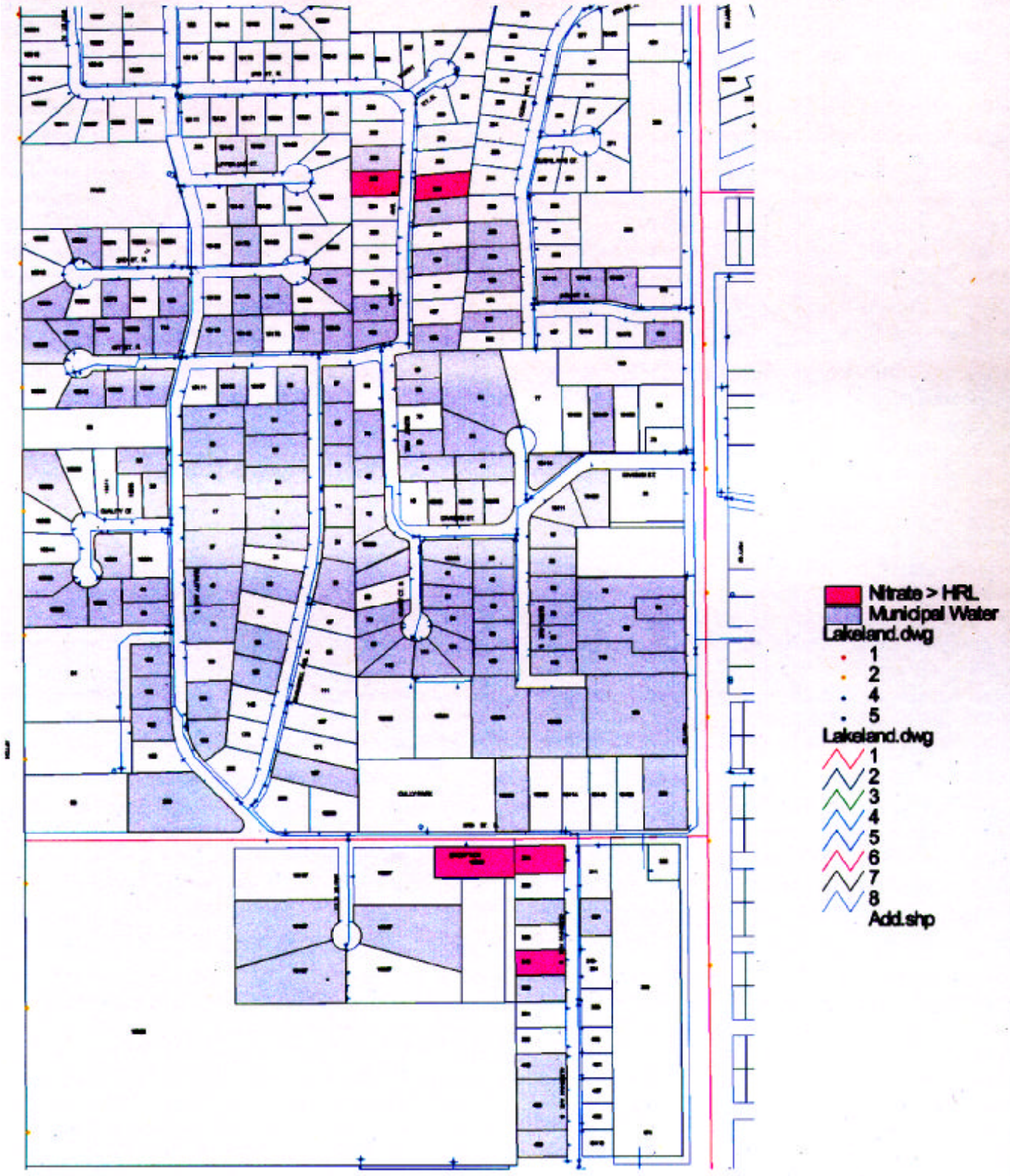


FOR INFORMATION PURPOSES ONLY
ACCURACY NOT ASSURED

ORIGINAL ADAPTATION: 1993
BARB HANSON AND RANDEE TWIMA

REVISION: 1995, DECEMBER
PAT LARSON

FIGURE 5
NITRATE HRL EXCEEDANCES



ATTACHMENT 2

DATA TABLES

LAKELAND RESIDENTIAL WELL SAMPLING RESULTS
MPCA SAMPLING NETWORK

Parameter		1,2,-DCA	1,1,1-TCA	TCE	PCE	cis-1,2-DCE	1,1,-DCA	Cancer
HRL		4	600	30	7	70	70	Hazard
Toxicological Endpoint		C	L	C	C	HS	K	Index
16035 1st St. N.	5/2/1994	0	1.1	1.7	0.7	0.6	na	0.16
16035 1st St. N.	5/1/1995	0	0.61	1.8	1.1	0.57	na	0.22
16035 1st St. N.	6/18/1996	0	1	2.1	1	0.9	na	0.21
16035 1st St. N.	7/16/1997	0	0.7	1.3	0.8	0.8	na	0.16
16035 1st St. N.	1/11/1999	0	0.5	1.2	0.7	0.9	0.2	0.14
16645 1st St. S.	10/19/1989	0	0.5	0	0	0		0.00
16645 1st St. S.	1/14/1991	0	0.3	0	0	0		0.00
16645 1st St. S.	5/2/1994	0	0.9	0.7	0	0		0.02
16645 1st St. S.	6/18/1996	0	0.9	0.9	0	0.3		0.03
16645 1st St. S.	7/16/1997	0	0.8	0.6	*	0.3		0.02
16645 1st St. S.	1/11/1999	0	1.1	1.3	0.3	0.9	0.2	0.09
16032 2nd St. N	5/2/1994	0	0	0	0	0		0.00
16032 2nd St. N	6/18/1996	0	0	0	0	0		0.00
16032 2nd St. N	7/17/1997	0	0	0	0	0		0.00
16032 2nd St. N	1/12/1999	0	0	0	0	0	0	0.00
16094 2nd St. N.	5/2/1994	0	0	0	0	0		0.00
16094 2nd St. N.	6/18/1996	0	0	0	0	0		0.00
16094 2nd St. N.	7/16/1997	0	0	0	0	0		0.00
16094 2nd St. N.	1/11/1999	0	0	0	0	0	0	0.00
16235 2nd St. N.	11/7/1989	0	0.6	0	0	0.2		0.00
16235 2nd St. N.	5/2/1994	0	0.5	1.5	0.5	0.5		0.12
16235 2nd St. N.	6/18/1996	0	0.4	1.2	0.5	0.3		0.11
16235 2nd St. N.	7/16/1997	0	0.3	0.7	0.4	0		0.08
16779 2nd St S.	9/21/1987	0	0.9	0	0	0		0.00
16779 2nd St S.	5/2/1994	0	1.5	2	0.6	0.8		0.15
16779 2nd St S.	5/1/1995	0	0.96	1.4	0.5	0.44		0.12
16779 2nd St S.	6/18/1996	0	1.6	2.1	0.8	0.8		0.18

All concentrations: ug/L (ppb)
C: cancer
L: liver
HS: hematological system

LAKELAND RESIDENTIAL WELL SAMPLING RESULTS
MPCA SAMPLING NETWORK

Parameter		1,2,-DCA	1,1,1-TCA	TCE	PCE	cis-1,2-DCE	1,1,-DCA	Cancer
HRL		4	600	30	7	70	70	Hazard
Toxicological Endpoint		C	L	C	C	HS	K	Index
16388 3rd St. S.	9/4/1987	0	1.2	0.7	0	0		0.02
16388 3rd St. S.	9/14/1989	0	0.5	0	0	0		0.00
16388 3rd St. S.	5/2/1994	0	0.9	0.9	0.2	0		0.06
16388 3rd St. S.	5/1/1995	0	0.34	0.32	0.21	0		0.04
16388 3rd St. S.	6/18/1996	0	0.3	0.3	0	0		0.01
16388 3rd St. S.	7/16/1997			denied request for sampling				
16388 3rd St. S.	1/11/1999	0	0.3	0.3	0.2	0	0	0.04
16044 Quality Ct.	5/3/1994	0	0	0	0	0		0.00
16044 Quality Ct.	6/18/1996	0	0	0	0	0		0.00
16044 Quality Ct.	7/16/1997	0	0	0	0	0		0.00
16044 Quality Ct.	1/8/1999	0	0	0	0	0	0	0.00
16066 Quality Ct.	6/18/1996	0	1	1.4	0.7	0.4		0.15
16066 Quality Ct.	7/16/1997	0	0.3	0.4	0.3	0		0.06
16066 Quality Ct.	1/8/1999	0	0	0.3	0.2	0	0	0.04
80 Quamwell	11/7/1988	0	0	0.2	0	0		0.01
80 Quamwell	11/7/1989	0	0	0	0	0		0.00
80 Quamwell	5/2/1994	0	1	1.1	0.5	0		0.11
80 Quamwell	5/1/1995	0	0.2	0.12	0	0		0.00
80 Quamwell Ave. S	6/18/1996	0	0.2	0.1	0	0		0.00
80 Quamwell Ave. S	7/16/1997	0	0	0	0	0		0.00
80 Quamwell Ave. S	1/1/1999			Not available for sampling.				
111 Quamwell	5/2/1994	0	0.6	0.7	0.2	0		0.05
111 Quamwell Ave. S.	6/18/1996	0	0	0.1	0	0		0.00
111 Quamwell	7/16/1997			Did not supply permission to sample				
111 Quamwell	1/8/1999	0	0.2	0.2	0.2	0	0	0.04
148 Quamwell	5/2/1994	0	0	0	0	0		0.00
148 Quamwell Ave. S.	6/18/1996	0	0	0	0	0		0.00
148 Quamwell	7/16/1997	0	0	0	0	0		0.00
148 Quamwell	1/8/1999	0	0	0	0	0	0	0.00
79 Quant Ave. N.	5/2/1994	0	0	0	0	0		0.00
79 Quant Ave. N.	6/18/1996	0	0	0	0	0		0.00

All concentrations: ug/L (ppb)
C: cancer
L: liver
HS: hematological system

LAKELAND RESIDENTIAL WELL SAMPLING RESULTS
MPCA SAMPLING NETWORK

Parameter		1,2,-DCA	1,1,1-TCA	TCE	PCE	cis-1,2-DCE	1,1,-DCA	Cancer
HRL		4	600	30	7	70	70	Hazard
Toxicological Endpoint		C	L	C	C	HS	K	Index
79 Quant Ave. N.	7/16/1997	0	0	0.3	0.3	0		0.05
79 Quant Ave. N.	1/11/1999	0	0	0	0	0	0	0.00
98 Quant Ave.	1/11/1999	Identified for sampling by MDH. Not sampled due to hookup to city water.						
444 Quinlan Ave. S.	12/17/1987	0	0.9	0.3	0	0		0.01
444 Quinlan	5/2/1994	0	1.7	2.3	0.7	0.5		0.18
444 Quinlan Ave. S.	6/18/1996	0	0	1.3	0.5	0.2		0.11
444 Quinlan Ave. S.	7/16/1997	0	0.7	0.9	0.5	0		0.10
444 Quinlan Ave. S.	1/11/1999	**On City water**						
152 Quehl Ave. N.	5/2/1994	0	0.2	0.6	0	0		0.02
152 Quehl Ave. N.	6/18/1996	0	0.2	0.5	0.3	0		0.06
152 Quehl Ave. N.	7/16/1997	0	0	0	0	0		0.00
152 Quehl Ave. N.	1/8/1999	0	*	0.3	0	0	0	0.01
16511 Division St.	5/2/1994	0	0.4	0.5	0	0		0.02
16511 Division St.	6/18/1996	0	0	0.5	0	0		0.02
16511 Division St.	7/16/1997	0	0.4	0.4	*	0		0.01
16511 Division St.	1/11/1999	0	0.5	0.7	0.2	0.2	0	0.05
34 Quamwell Ave S.	1/8/1999	0	0.6	1	0.7	0.4	0	0.13
16111 1st Ave. N.	1/14/1999	0	0	0.4	0.2	0.2	0	0.04

*: peak present below report level of 0.2 ug/L

All concentrations: ug/L (ppb)
C: cancer
L: liver
HS: hematological system

TABLE 29

VOC Concentrations - Lakeland Private Wells
May 1995

Tower Asphalt
Lakeland, Minnesota

ADDRESS		16035 1st N.	80 Quamwell	16388 3rd S.	16779 2nd S.	444 Quinlan S.
	HRL	PW-1	PW-2	PW-3	PW-4	PW-5
1,1,2,2-tetrachloroethene (PCE)	7	1.1	<0.08	0.21	0.50	0.47
1,1,2-trichloroethene (TCE)	30	1.8	0.12	0.32	1.4	1.1
cis-1,2-dichloroethene	70	0.57	<0.2	<0.2	0.44	<0.2
1,1,1-trichlorothane (TCA)	600	0.61	0.20	0.34	0.96	0.68
1,1-dichloroethane (DCA)	70	<0.18	<0.18	<0.2	<0.2	<0.2
Nitrate	10	9.0	26	28	34	28
Hazard Index - cancer	1.0	0.2	0.1	0.1	0.1	0.1

Concentrations of VOCs in ug/l.
Concentrations of Nitrate in mg/l.

TABLE 30

Comparison of Health Risk
(1987 - 1990 Data)

Tower Asphalt
Lakeland, Minnesota

ADDRESS	RALs		HRLs	
	RAL Exceedance for PCE	≥ 4 VOCs	Hazard Index for Cancer	Risk Exceedance
16038 1st Street N.		X	1.3	X
16060 1st Street N.		X	0.3	
16087 1st Street N.		X	0.9	
16088 1st Street N.	X	X	2.0	X
16118 1st Street N.		X	0.9	
16135 1st Street N.		X	1.3	X
16409 1st Street S.	X	X	0.7	
16555 1st Street S.		X	0.3	
16199 2nd Street N.		X	0.4	
16554 2nd Street S.		X	0.3	
16660 2nd Street S.		X	0.2	
16715 4th Street S.		X	0.5	
16725 4th Street S.		X	0.3	
16303 Division St.		X	0.6	
16330 Division St.		X	0.5	
16333 Division St.		X	0.8	
16350 Division St.		X	0.4	
16370 Division St.		X	0.8	
16411 Division St.		X	1.0	X
16414 Division St.		X	0.4	
16433 Division St.		X	0.5	
17 Quality Avenue N.		X	0.5	
30 Quality Avenue N.		X	0.7	
27 Quality Avenue S.		X	0.4	

TABLE 30 (continued)

Comparison of Health Risk
(1987 - 1990 Data)

Tower Asphalt
Lakeland, Minnesota

ADDRESS	RALs		HRLs	
	RAL Exceedance for PCE	≥ 4 VOCs	Hazard Index for Cancer	Risk Exceedance
14 Quamwell Avenue N.		X	0.7	
34 Quamwell Avenue N.		X	1.2	
53 Quamwell Avenue N.		X	0.5	
60 Quamwell Avenue N.		X	0.6	
83 Quamwell Avenue N.		X	1.1	X
94 Quamwell Avenue N.		X	1.1	X
97 Quamwell Avenue N.		X	0.7	
9 Quamwell Avenue S.		X	0.5	
16 Quamwell Avenue S.		X	0.4	
21 Quamwell Avenue S.		X	0.5	
34 Quamwell Avenue S.		X	0.5	
39 Quamwell Avenue S.		X	1.2	X
56 Quamwell Avenue S.		X	0.4	
12 Quant Avenue N.	X	X	2.1	X
42 Quant Avenue N.		X	0.6	
69 Quant Avenue N.		X	1.1	X
74 Quant Avenue N.		X	1.2	X
89 Quant Avenue N.		X	0.4	
98 Quant Avenue N.	X	X	1.8	X
99 Quant Avenue N.		X	0.2	
160 Quant Avenue N.		X	0.3	
61 Quant Court S.		X	1.0	X
81 Quant Court S.		X	0.8	
101 Quant Court S.		X	0.5	
300 Queenan Avenue S.		X	0.3	
44 Quehl Avenue S.	X	X	1.4	X

TABLE 30 (continued)

Comparison of Health Risk
(1987 - 1990 Data)

Tower Asphalt
Lakeland, Minnesota

ADDRESS	RALs		HRLs	
	RAL Exceedance for PCE	≥ 4 VOCs	Hazard Index for Cancer	Risk Exceedance
13 Quehl Avenue S.		X	0.9	
20 Quehl Avenue S.		X	0.6	
33 Quehl Avenue S.		X	0.3	
40 Quehl Avenue S.		X	0.6	
53 Quehl Avenue S.		X	0.4	
60 Quehl Avenue S.		X	0.6	
73 Quehl Avenue S.		X	0.6	
93 Quehl Avenue S.		X	0.6	
100 Quehl Avenue S.		X	0.7	
113 Quehl Avenue S.		X	0.5	
355 Quinlan Avenue S.		X	0.4	
360 Quinlan Avenue S.		X	0.4	
380 Quinlan Avenue S.		X	0.5	
391 Quinlan Avenue S.		X	0.6	
78 St. Croix Trail South		X	0.9	
84 St. Croix Trail South		X	0.8	
92 St. Croix Trail South		X	0.3	
110 St. Croix Trail South		X	0.6	
143 St. Croix Trail South		X	0.4	

Notes:

Based on water quality data collected in 1987-1990 by MPCA

RAL = Recommended Allowable Limits, Release No. 2 November 1988.
HRL = Health Risk Limits, December 1994
HI = Hazard Index

TABLE 31

Hazard Index Trends
in Lakeland Private Wells

Tower Asphalt
Lakeland, Minnesota

ADDRESS	1987	1988	1989	1990
16060 1st Street N.	0.7/0.5	--	0.3	--
16087 1st Street N.	0.4/0.8	0.6	0.9	--
16088 1st Street N.	1.8	2.0	--	--
16118 1st Street N.	0.9/0.6	--	--	--
16170 2nd Street N.	0.5	0.2	--	--
16715 4th Street S.	0.3	--	0.5	--
16433 Division	--	0.5	--	<0.1
30 Quality Avenue N.	0.2/0.1	0.7	--	--
98 Quant Avenue N.	1.1	1.8	--	--
78 St. Croix Trail S.	0.5	--	--	0.9

There are no significant comparative Hazard Indices for the years 1991 to present.

A dash (--) indicates that no samples were taken.

Multiple values in a single year indicate the hazard index for multiple sampling events.

TABLE 28

Nitrate Trends - Private Wells in Southern Plume Area

Tower Asphalt
Lakeland, Minnesota

AGGREGATE TREND

DATE	Average Concentration
1977-1981	6.0 (14 samples, ranging from 4.4 to 10.4)
1982-1986	6.1 (30 samples, ranging from 3.4 to 12.0)
1987-1991	6.8 (10 samples, ranging from 2.8 to 9.0)
1992-1995	29.0 (4 samples, ranging from 26 to 34)

INDIVIDUAL TREND

Address	Date	Concentration
16615 1st Street South	10/88	2.8
	11/88	5.9
16388 3rd Street South	09/86	7.5
	05/95	28
16850 Division	08/83	8.3
	08.87	8.3
34 Quamwell Avenue South	03/84	4.0
	10/86	4.7
89 Quant Avenue North	03/77	4.8
	11/82	4.9
	08/85	7.0
20 Quehl Avenue South	09/81	6.2
	04/86	5.9

Note:
All concentrations in mg/l.
All wells are completed int he Quaternary (sand and gravel) aquifer.

ATTACHMENT 3

VINYL CHLORIDE REFERENCE

Vinyl Chloride Loss during Laboratory Holding Time

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Because vinyl chloride is a potent human carcinogen, it is important that analytical results from groundwater samples accurately reflect levels of exposure to groundwater users. This study investigated the current allowable holding time of 14 days to determine if vinyl chloride is lost from samples during this time. Samples containing an initial concentration of 2 μg/liter of vinyl chloride showed progressive, increasing losses when held for 1, 2, 7, and 14 days. Due to the inherent variability of low-level laboratory results, the most statistically significant loss ($\alpha = 0.05$) was seen for samples held for 14 days. No statistically significant differences in degradation pattern were noted between analytical detectors used (PID versus Hall) or sample type (lab versus field). There also was a loss of vinyl chloride observed during sample collection and handling. These results suggest that analytical variability at low concentrations and the establishment of health-based guidelines near the analytical detection limit require multiple samples be collected from a single location when highly accurate results are needed. These findings should be considered in public health exposure assessments and the implementation of health-based recommendations at sites with vinyl chloride groundwater contamination. © 1996 Academic Press, Inc.

INTRODUCTION

Vinyl chloride is a potent human carcinogen and a common groundwater contaminant near hazardous waste sites. The guidelines for drinking water supplies containing vinyl chloride in Minnesota (USEPA, 1993; MDH, 1994) are nearly equivalent to typically reported analytical detection limits (ATSDR, 1993). Vinyl chloride has been found at 458 of the 1300 federal Superfund sites (ATSDR, 1993) and is commonly identified at levels above its regulatory guidelines. Efforts to protect users of aquifers contaminated by vinyl chloride rely on analytical results to estimate human exposure. This makes it important to confidently determine that analytical results accurately reflect levels of vinyl chloride exposure.

The U.S. Environmental Protection Agency (USEPA) recommends that preserved water samples tested for vinyl chloride be analyzed within 14 days of collection (USEPA, 1988). In our experience, water samples analyzed immediately after collection seemed consistently higher than similar samples that were held for longer periods. This raised the concern that samples which are held for even a small portion of the holding time may underestimate both the vinyl chloride concentration and the potential human exposure. This, in turn, could result in an underestimation of the health threat to users of contaminated groundwater. The objective of this study was to determine if a significant amount of vinyl chloride was lost from water samples during the 14-day holding period.

METHODS

Two types of water samples were tested: laboratory-prepared water containing a known concentration of vinyl chloride ("lab samples") and groundwater samples collected from a single well ("field samples"). As an extraction well for a groundwater treatment system, this well is pumped continuously and has historically yielded groundwater consistently containing low part per billion levels of vinyl chloride. The concentration in the lab samples was chosen to be similar to those recently found in the well (1.5 μg/liter).

As shown in Fig. 1, three replicates of 20 field samples and 20 lab samples were collected in clean 40-ml glass vials with Teflon-lined septa. Samples within a replicate were numbered corresponding to their order of filling. Sampling procedures followed the techniques typically used in environmental investigations (MPCA, 1986). All samples were preserved with a biocide, adjusted to pH less than 2, and immediately refrigerated at 4°C until testing.

Both the field and lab samples were systematically assigned to four different holding time groups. Groups of five field samples and five lab samples each were

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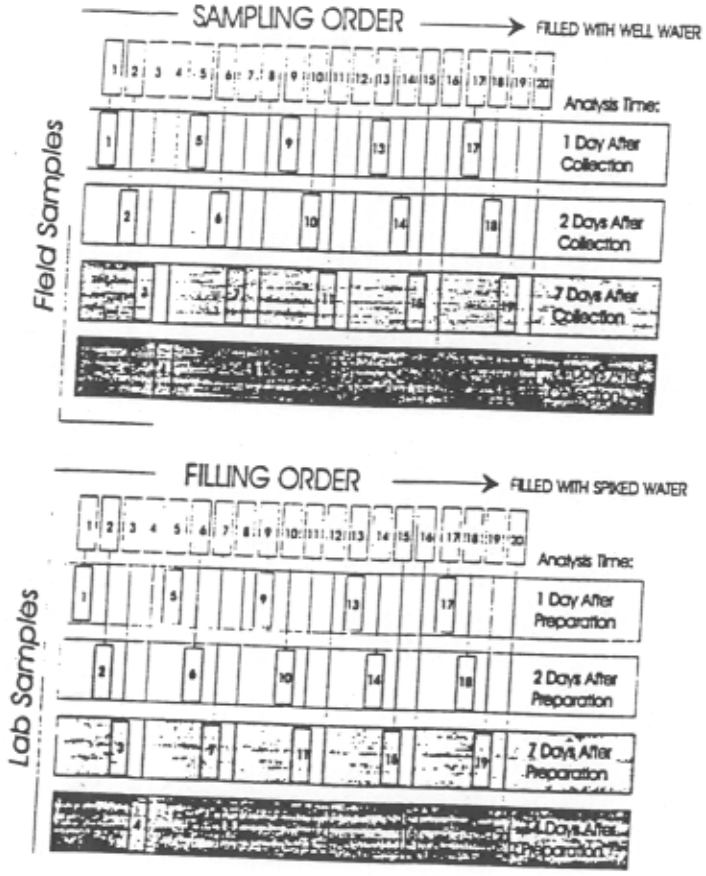

FIG. 1. Sampling procedure.

analyzed at 1, 2, 7, and 14 days after collection (Fig. 1). Laboratory internal control samples consisted of laboratory standards and spiked samples. Blank and matrix spike data did not show sample contamination or a significant matrix effect on instrument performance.

Each sample was analyzed for vinyl chloride using both a photoionization detector (PID) and a Hall detector (Hall). Data from each detector were reported and compared separately using Student's t test. A Tracor 540 gas chromatograph was used along with a Tekmar TURBOcool option and EPA method 502.2 (USEPA, 1989). Chromatographic conditions were Restek Corp. 105-m × 0.53-mm-i.d. column with 3-μm film, trap temperature during purge at −20°C, trap packing Supelco Vocarb 3000, and purge time of 3 min; column program was initially at 40°C for 10 min, then 10°C per minute to 200°C, and held for 5 min.

RESULTS

The percentage loss of vinyl chloride for the lab and field samples versus holding time is plotted in Fig. 2. Data from replicates were combined to yield a data set of 15 samples (n = 15) for each detector and sample holding time group. Approximately 40% of the vinyl

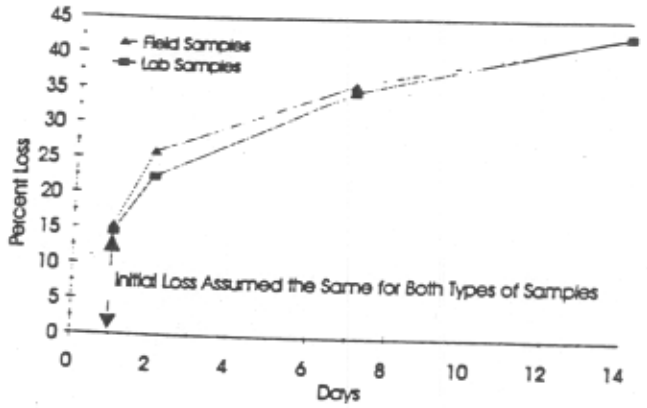

FIG. 2. Percentage loss over holding time.

chloride initially present was lost over the entire 14-day holding time, with roughly half (25%) of the loss occurring in the first 2 days. The decrease in vinyl chloride concentrations observed is statistically significant (α = 0.05). The same trend of vinyl chloride loss was observed for both types of analytical detector.

The standard deviations of the combined results ranged from 0.02 to 0.17 μg/liter for the lab samples and from 0.07 to 0.29 μg/liter for the field samples. Daily standards prepared in the lab showed similar variability, suggesting that most of the variability was a result of the analytical methods (rather than a result of sample handling). This high degree of relative variability is common for vinyl chloride samples analyzed in this range and may raise concerns about the reliability of using a single sample to make public health determinations.

Figure 3 shows an analysis of concentration versus filling order. The major cyclical trend is due to the varying holding times for sequential sample bottle numbers. The figure suggests that there may be two other types of vinyl chloride loss occurring during the holding

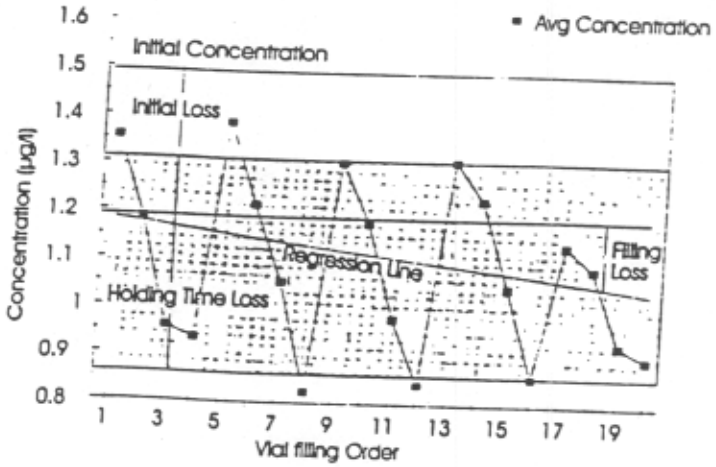

FIG. 3. Types of losses.

time: (a) an initial loss of about 0.22 μg/liter (15%) that affects the results from all sample vials, regardless of origin or detector; and (b) a progressively increasing handling loss of up to 0.15 μg/liter (10%) which is shown by the regression line. The initial loss could only be determined using laboratory samples where the initial concentration is known (prepared spike). This portion of the loss may be laboratory related, such as measurement error, handling or headspace loss, or a factor common to all samples such as binding to glass, photodegradation, or loss through the septa. The handling loss is likely a result of increasing duration of sample exposure to air with increasing sample number (e.g., water in vial 20 was exposed to air longer and showed a greater loss than water in vial 1 since each was poured from the same supply).

DISCUSSION

Health-based standards for vinyl chloride are very low because it is rated as a Class A carcinogen with a relatively high estimated oral cancer slope factor of 1.9 $(mg/kg/day)^{-1}$ (USEPA, 1994). The U.S. EPA Maximum Contaminant Level, which is the value used for vinyl chloride in municipal water supply systems, is 2 μg/liter (based on the analytical detection limit; USEPA, 1993). The Minnesota Department of Health (MDH) has established a health-based guideline for private drinking water supplies of 0.2 μg/liter (based on cancer potency slope and a 10^{-5} risk; MDH, 1994). These standards are roughly equivalent to reported analytical detection limits in water (ATSDR, 1993). Due to the decrease in precision which occurs as concentrations approach the detection limit, accurate estimates of ambient water concentrations from a single sample are more difficult to obtain at lower concentrations.

The physicochemical characteristics of vinyl chloride and its environmental fate may eliminate several possible explanations for the observed loss. Although vinyl chloride has a very high saturation vapor pressure (2530 mm Hg at 20°C) and is subject to partitioning into an air head space [Henry's Law Constant of 1.2 $(atm\text{-}m^3)/mol$ at 10°C], all samples were thoroughly checked to ensure that any air bubbles were removed. Although under certain circumstances vinyl chloride readily biodegrades (ATSDR, 1993), this pathway seems unlikely given that all samples were acidified and treated with biocide. The samples were kept in a darkened refrigerator to minimize photochemical degradation (EPA, 1986). Sorption of some organic chemicals onto the materials of sample containers has been observed (Bradbury *et al.*, 1987), but the low octanol–water partitioning coefficient ($\log K_{ow} = 1.36$) for vinyl chloride indicates that this would be negligible for the concentrations used in this study (per equation 5.8.4 in Manahan, 1994).

The most common source of vinyl chloride in groundwater at hazardous waste sites is the anaerobic dehalogenation of 1,1,2-trichloroethene, tetrachloroethene, and 1,1,1-trichloroethane (ATSDR, 1993). Therefore, it can be present in groundwater at sites where pure vinyl chloride was not used or disposed and may be overlooked when developing a list of contaminants of concern. In addition, if an analytical technique is used which has a detection limit above 2 μg/liter, a significant complete exposure pathway may be missed and potential risks from a site underestimated.

Since significant public health actions, such as imposing drinking water restrictions or installing expensive treatment/removal systems, often hinge on limited analytical results, it is crucial to obtain the most accurate and precise measurements possible. For vinyl chloride, this can be accomplished by collecting more than one sample from a well, taking care to ensure that sample contact with the air is minimized, and using sufficiently sensitive analytical techniques. It is important for both risk assessors and risk managers to recognize the uncertainties in sample collection and analysis when dealing with analytical data from groundwater drinking water supplies potentially contaminated with vinyl chloride.

CONCLUSIONS

A statistically significant amount of vinyl chloride was lost from water samples between the time of collection and analysis. This loss increased to 40% of the initial concentration when held for 14 days prior to analysis. Therefore, immediate testing of samples is warranted where low part per billion concentrations of vinyl chloride may be present in drinking water (e.g., when concentrations may be near health-based standards). Moreover, the results of immediate analyses are more representative of actual exposure concentrations than those from samples held for longer times.

In addition to loss during holding time, this study suggests that there may be significant loss of vinyl chloride due to the sampling and handling processes. Therefore, sampling and analysis techniques should be reviewed to minimize sample exposure to the air.

Due to analytical variability at low concentrations, collection and analysis of multiple water samples from a single location are also warranted when highly accurate results are needed (e.g., when sample concentrations are near health-based guidelines or the analytical detection limit).

Since significant public health actions, such as imposing drinking water restrictions or installing expensive treatment/removal systems, often hinge on limited analytical results, it is crucial to obtain the most accurate and precise measurements possible. Both risk assessors and managers need to be aware of the uncertainty associated with reported vinyl chloride results in

order to make informed and appropriate public health decisions.

Although vinyl chloride was lost from samples, this study does not identify the mechanism of the loss. Some possible explanations may be volatilization (either into ambient air during sampling and analysis or directly through the sample bottle septa), microbial breakdown in the natural water, or chemical degradation. Additional analysis is currently being conducted to further characterize the mechanism of the observed loss.

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