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Prepared in cooperation with the U.S. Department of Energy

# **Evaluation of Sample Preservation Methods for Analysis of Selected Volatile Organic Compounds in Groundwater, Idaho National Laboratory**

Scientific Investigations Report 2022–5076

**Cover.** Eastern Snake River Plain as seen looking northwest towards the Lost River Range, Idaho.  
Photograph by Kerri C. Treinen, U.S. Geological Survey, May 2022.

# **Evaluation of Sample Preservation Methods for Analysis of Selected Volatile Organic Compounds in Groundwater at the Idaho National Laboratory, Idaho**

By Kerri C. Treinen and Roy C. Bartholomay

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**U.S. Department of the Interior  
U.S. Geological Survey**

## U.S. Geological Survey, Reston, Virginia: 2022

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## Conversion Factors

U.S International System of Units to U.S. customary units

Multiply	By	To obtain
Length		
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
meter (m)	1.094	yard (yd)
Area		
square kilometer (km <sup>2</sup> )	0.3861	square mile (mi <sup>2</sup> )
Volume		
liter (L)	33.81402	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:  
 $^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$ .

## Datums

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29).

Horizontal coordinate information referenced to the North American Datum of 1927 (NAD 27).

## Supplemental Information

Concentrations of chemical constituents in water are given in micrograms per liter (µg/L).

## Abbreviations

ATRC	Advanced Test Reactor Complex
DOE	U.S. Department of Energy
ESRP	eastern Snake River plain
HCl	hydrochloric acid
INL	Idaho National Laboratory
INLPO	Idaho National Laboratory Project Office
INTEC	Idaho Nuclear Technology and Engineering Center
MCL	maximum contaminant levels
MRL	minimum reporting levels
NAD	normalized absolute difference
NWQL	U.S. Geological Survey National Water Quality Laboratory
QA	quality assurance
QC	quality control
RPD	relative percent difference
RWMC	Radioactive Waste Management Complex
TAN	Test Area North
USGS	U.S. Geological Survey
VOC	volatile organic compound



# Evaluation of Sample Preservation Methods for Analysis of Selected Volatile Organic Compounds in Groundwater at the Idaho National Laboratory, Idaho

By Kerri C. Treinen and Roy C. Bartholomay

## Abstract

During 2020, water samples were collected from 25 wells completed in the eastern Snake River Plain aquifer and from 1 well completed in perched groundwater above the aquifer at the Idaho National Laboratory to determine the effect of different sample-preservation methods on the laboratory determinations of concentrations of volatile organic compounds. Paired-sample sets were collected at each well. One sample in each set was preserved with hydrochloric acid, and one sample without. Both samples were chilled after collection and during shipping to the laboratory for analysis. The samples were analyzed for 61 volatile organic compounds at the U.S. Geological Survey National Water Quality Laboratory in cooperation with the U.S. Department of Energy. A comparison of the reproducibility of the analyses of co-located unpreserved and preserved samples by a relative percent difference method determined that all sample pairs were statistically equivalent. Using a normalized absolute difference method, 81 percent of the analyses were found to be statistically equivalent. This study confirms that the results of analyses of historical collected samples, which were preserved by chilling only, are statistically comparable to the analyses of samples being currently collected and preserved by both hydrochloric acid and chilling, and thus are valid for use in future geochemical evaluations.

## Introduction

The Idaho National Laboratory (INL), encompassing about 890 square miles (mi<sup>2</sup>) of the eastern Snake River Plain (ESRP) in southeastern Idaho, is operated by the U.S. Department of Energy (DOE) ([fig. 1](#)). INL facilities are used in the development of peacetime atomic-energy applications,

nuclear safety research, defense programs, and advanced energy concepts. The disposal of liquid and solid waste at the laboratory has resulted in the presence of several waste constituents in water in the ESRP aquifer underlying the INL. The U.S. Geological Survey (USGS) INL Project Office, in cooperation with the DOE, provides an independent assessment of the occurrence, migration, and fate of waste constituents in water in the ESRP aquifer.

For more than 70 years, the USGS has worked in cooperation with DOE to help determine: (1) the quality and quantity of water for human consumption, (2) the suitability of the water for supporting construction and cooling of facilities, (3) location and migration of contaminants from the ESRP aquifer and in perched groundwater above the aquifer, (4) sources of recharge to the aquifer, (5) requirements of a monitoring network to detect contaminants migrating beyond the INL boundaries, and (6) processes controlling the migration of contaminants and naturally occurring constituents in the aquifer (Ackerman and others, 2010).

Wastewater containing volatile organic compounds (VOCs) was directly injected into the aquifer through disposal wells at Test Area North (TAN) and at the Idaho Nuclear Technology and Engineering Center (INTEC) ([fig. 1](#)). Wastewater containing VOCs was discharged into infiltration ponds at the Advanced Test Reactor (ATR) Complex, and an estimated 88,400 gallons of organic waste were buried before 1970 at the Radioactive Waste Management Complex (RWMC; [fig. 2](#)) (Mann and Knobel, 1987; Maimer and Bartholomay, 2016; Bartholomay and others, 2020). Background concentrations of VOCs in the ESRP aquifer at the INL are generally less than 2 micrograms per liter (µg/L) (Orr and others, 1991).

2 Evaluation of Preservation Methods for Analysis of Volatile Organic Compounds in Groundwater

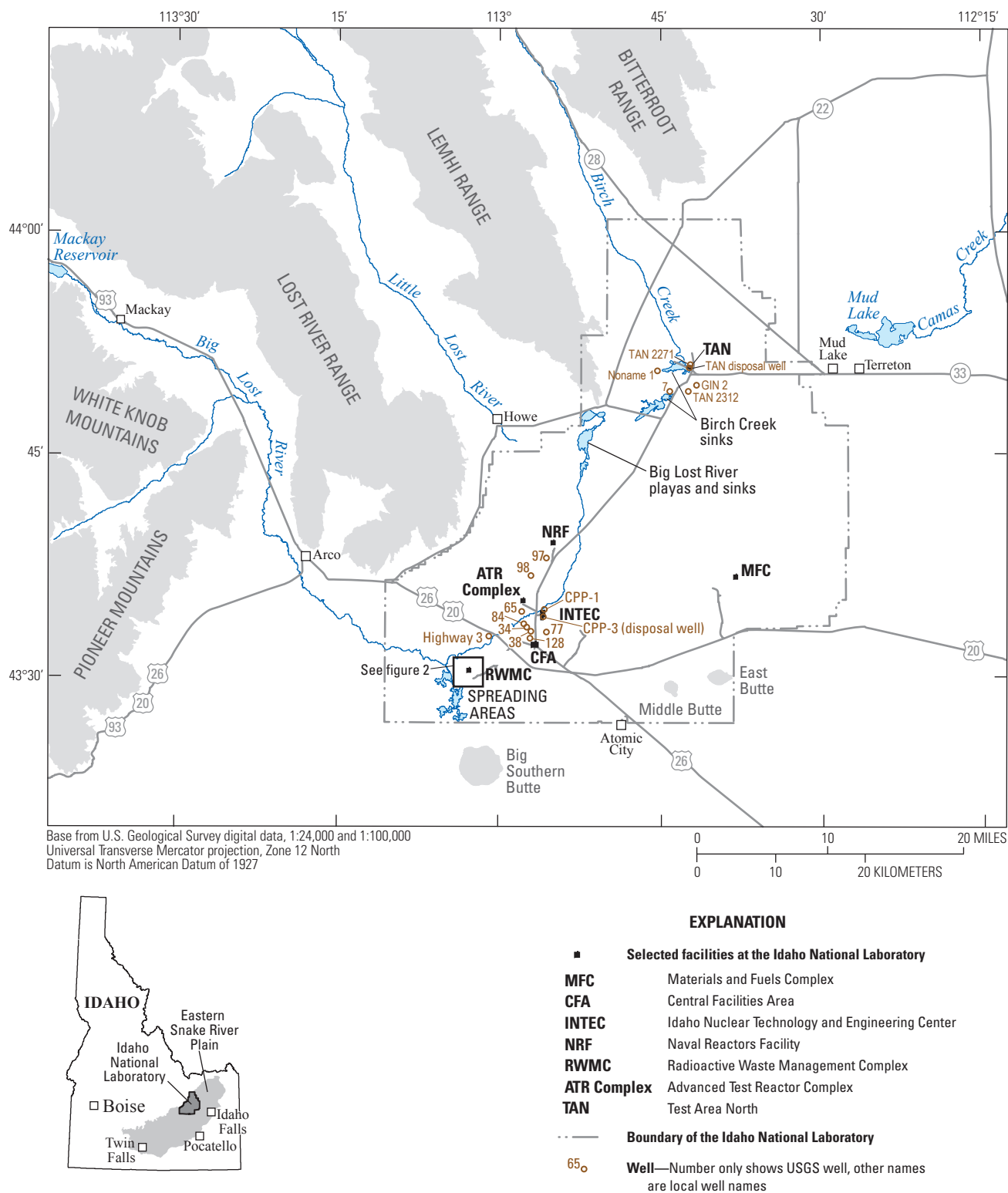
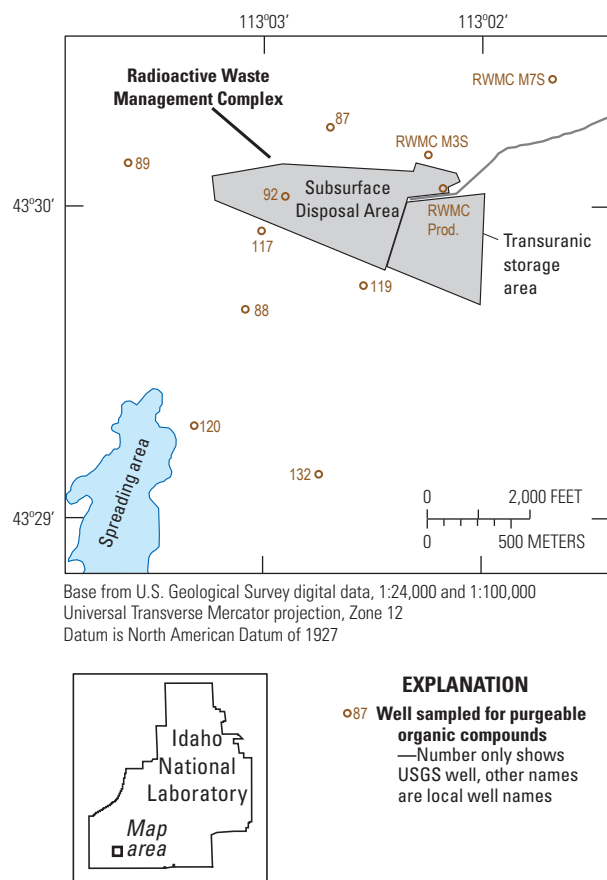


Figure 1. Location of the Idaho National Laboratory, selected facilities at the Idaho National Laboratory, and locations of wells sampled for this study in 2020.



**Figure 2.** Location of wells near the Radioactive Waste Management Complex at the Idaho National Laboratory sampled for analyses of volatile organic compounds for this study in 2020.

The INL Project Office collects water samples for VOC analyses as part of the ongoing USGS assessment of water quality in the ESRP aquifer. Sixty-one VOCs are routinely analyzed in samples collected from existing wells at and near the Test Area North, ATR Complex, INTEC and RWMC and from new wells drilled at the INL. In the late 1980s and early 1990s, the VOC analytical method used at the USGS National Water Quality Laboratory (NWQL) required raw, unfiltered water, chilled for shipment to the laboratory for analysis. In the mid-to-late 1990s, the laboratory suggested acidifying groundwater samples in the field with hydrochloric acid (HCl) for sample preservation (app. 1; Connor and others, 1998). At that time, however, the NWQL continued to accept raw, unfiltered samples from the field and analyzed them as received without adjusting the pH of the sample upon arrival at the laboratory.

To be consistent with historical (pre-mid-1990s) sample collection methods, the INL Project has continued to send only raw (unacidified), unfiltered, and chilled samples to the laboratory for VOC analysis, but are now considering adding acid to the samples in the field to meet this requirement of the laboratory.

## Purpose and Scope

This report describes a quality-assurance (QA) study in which the individual water samples of a paired set of samples collected in 2020 from 26 wells at INL were processed and handled differently. One of the samples in each set was chilled upon collection and during shipment to the laboratory for analysis of VOCs; this sample will be referred to in this report as “unpreserved.” The other sample in each set was acidified with HCl and then chilled upon collection; this sample will be referred to here as “preserved.” Results of the analyses were then compared in statistical tests to evaluate reproducibility between VOC concentrations in the unpreserved and preserved samples in each sample set. The data described in this study can be found in the USGS National Water Information System (U.S. Geological Survey, 2016).

## Geohydrologic Setting

The INL is located on the west-central part of the eastern Snake River Plain, a northeast-trending structural basin about 200 miles (mi) long and 50–70 mi wide. The ESRP aquifer is one of the most productive aquifers in the United States (U.S. Geological Survey, 1985, p. 193). Groundwater generally moves from northeast to southwest and discharges to springs along the Snake River downstream from Twin Falls, Idaho, about 100 mi southwest of the INL. Groundwater moves horizontally through basalt interflow zones and vertically through joints and interfingering edges of basalt flows. Infiltration of surface water, pumping from wells completed in the aquifer, geohydrologic conditions, and seasonal fluxes of recharge and discharge locally affect the movement of groundwater (Garabedian, 1986). The aquifer is recharged primarily by infiltration of applied irrigation water, infiltration of stream-flow, groundwater inflow from adjoining mountain drainage basins, and infiltration of precipitation (Ackerman and others, 2006). At the INL, depth to water in wells completed in the ESRP aquifer ranges from about 225 feet (ft) below land surface in the northern part of the INL to more than 900 ft below land surface in the southeastern part of the INL (Bartholomay and others, 2020, p. 20).

## Previous Investigations

In the mid-1990s, the USGS conducted a study to investigate a suggested change to the protocol for collection and field processing of water samples for laboratory analyses of VOCs. The standard protocol at that time was to simply chill the raw samples for shipment to the laboratory. The suggested change was to add HCl to the samples as a preservative upon collection and then chilling them. A comparison of the results of analyses of paired sets of samples processed by the different field techniques indicated that the addition of HCl along with chilling of the samples did not have a statistically significant effect on the concentration of VOCs determined

by the laboratory in samples from multiple sources, including groundwater, surface water, stormwater runoff, and sewage effluent. On the basis of those findings, the standard protocol for field processing of samples for VOC analyses was updated to include the addition of HCl along with chilling (app. 1; Connor and others, 1998).

In addition to the type of study mentioned above, the USGS INL Project Office has a history of performing investigations to assure the validity and accuracy of water-quality data collected at the INL. Investigations to determine variability and bias in laboratory analytical results (concentrations) of individual constituents were summarized by Wegner (1989), Williams (1996, 1997), and Rattray (2012, 2014). Additional QA studies that focus on sample collection and field processing techniques by USGS INL Project Office personnel include:

- An evaluation of field sampling and preservation methods for strontium-90 analyses (Cecil and others, 1989);
- A comparison of pump types used for collecting samples for analysis of VOCs (Knobel and Mann, 1993);
- An analysis of tritium and strontium-90 concentrations in water samples from wells after purging different borehole volumes (Bartholomay, 1993);
- An analysis of the effects of multiple preservation types on laboratory determined nutrient concentrations (Bartholomay and Williams, 1996);
- An analysis of two analytical methods to determine gross alpha- and beta-particle activity in water samples (Bartholomay and others, 1999);
- An evaluation of well-purging effects on laboratory analytical results (Knobel, 2006);
- An evaluation of 2009–11, 2012–15, and 2016–18 QA data for routine sampling of groundwater at INL (Davis and others, 2013; Bartholomay and others, 2017; Bartholomay and others, 2020); and
- An evaluation of the 2006–08, 2009–13, and 2014–18 multilevel monitoring system QA data (Bartholomay and Twining, 2010; Bartholomay and others, 2015; Twining and others, 2021).

## Study Methods

This study evaluated the field-preservation of water samples, a targeted-variable associated with data generation (Mueller and others, 2015). For the purposes of this report, sequentially collected samples are defined as paired-samples.

The unpreserved sample was collected first, followed by collection of the preserved sample, as a sequential replicate sample pair.

The study was designed to address variability associated with hydrologic and chemical conditions and factors including the following: (1) the samples were collected over a wide geographic range at the INL; (2) they were collected from multiple depths within the ESRP aquifer as well as from a perched groundwater zone; and (3) they were collected in different seasons and under different hydrologic conditions. Overall, the subset of wells sampled and the samples collected from them in this current study are a representative cross-section of the groundwater conditions and locations that have been historically sampled by the INL Project Office for VOC concentrations during a period when the sample processing did not include preservation by the addition of HCl.

## Sample Collection and Processing

To evaluate the effect of different sample preservation methods on the reproducibility of laboratory-determined VOC concentrations, 37 paired-samples were collected from 25 wells completed in the ESRP aquifer, and 1 well completed in a perched groundwater zone above the aquifer (figs. 1, 2). Discrete samples were pumped from wells equipped with permanently installed submersible pumps through in-line stainless-steel sampling pipes attached to the well head or spigots. The samples were collected according to procedures described in the USGS National Field Manual (with the exception of adding HCl as a preservative for VOC analyses) (U.S. Geological Survey, 2018; Connor and others, 1998, and further described in the INLPO field methods and quality-assurance plan (Bartholomay and others, 2014).

Both unpreserved and preserved samples for the analysis of VOCs were collected in clean 40-mL borosilicate amber vials (VOC vials). The historical and current VOC sample collection and processing method for the INL Project Office is to fill the vials from the bottom up and fill to overflowing, capping immediately without any headspace, and chilling (historically collected unpreserved samples). The preserved sample was processed in the mobile field laboratory by adding, dropwise from a Teflon squeeze bottle, a concentrated solution of (1:1) HCl supplied by the NWQL. In-house testing at the INLPO prior to the field sampling determined that approximately five drops of HCl were necessary to achieve a sample pH of 2. Both unpreserved and preserved samples were kept at  $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$  by chilling immediately after collection, and during shipment to the NWQL. Samples are shipped by overnight-delivery mail in a sealed ice chest and are typically sent to the laboratory within five days of collection (Maimer and Bartholomay, 2016).

**Table 1.** Maximum contaminant levels and minimum reporting levels of selected volatile organic compounds in water.

[Analyses performed by the U.S. Geological Survey National Water Quality Laboratory using an analytical method equivalent to U.S. Environmental Protection Agency method 524.2 (Rose and others, 2016). MCLs were established pursuant to the recommendations of the U.S. Environmental Protection Agency (2020) for community water systems and are included for comparison purposes only. MRLs are from the Laboratory Information Management System (LIMS) used by the National Water Quality Laboratory, U.S. Geological Survey. Units are in micrograms per liter ( $\mu\text{g/L}$ ). **Abbreviations:** MCL, maximum contaminant level; MRL, minimum reporting level. **Symbols:** --, MCL has not been established or proposed; \*, total trihalomethanes-which include bromoform, dibromochloromethane, chloroform, and dibromomethane in community water systems serving 10,000 or more persons cannot exceed 80  $\mu\text{g/L}$  (U.S. Environmental Protection Agency, 2020)]

Compound	MCL	MRL	Compound	MCL	MRL
Acrylonitrile	--	2.5	Trichloroethylene (-ethene)	5	0.1
Benzene	5	0.1	Trichlorofluoromethane	--	0.2
Bromobenzene	--	0.2	Trichloromethane (Chloroform)	*	0.1
Bromochloromethane	--	0.2	Vinyl chloride	2	0.2
Bromodichloromethane	*	0.2	Xylenes, all isomers	10,000	0.3
Bromomethane	--	0.3	1,1,1,2-Tetrachloroethane	--	0.2
Butylbenzene	--	0.2	1,1,1-Trichloroethane	200	0.1
Chlorobenzene (mono-)	100	0.1	1,1,2,2-Tetrachloroethane	--	0.2
Chloroethane	--	0.2	1,1,2-Trichloroethane	5	0.2
Chloromethane	--	0.2	1,1,2-Trichlorotrifluoroethane	--	0.1
cis-1,2-Dichloroethene (-ethylene)	70	0.1	1,1-Dichloroethane	--	0.1
cis-1,3-Dichloropropene	--	0.2	1,1-Dichloroethene (-ethylene)	7	0.1
Dibromochloromethane	*	0.2	1,1-Dichloropropene	--	0.2
Dibromomethane	--	0.2	1,2,3-Trichlorobenzene	--	0.2
Dichlorodifluoromethane	--	0.2	1,2,3-Trichloropropane	--	0.2
Dichloromethane	5	0.2	1,2,4-Trichlorobenzene	70	0.2
Ethylbenzene	700	0.1	1,2,4-Trimethylbenzene	--	0.2
Hexachlorobutadiene	--	0.2	1,2-Dibromo-3-chloropropane	--	0.5
Isopropylbenzene	--	0.2	1,2-Dibromoethane	--	0.2
Methyl tert-butyl ether (MTBE)	--	0.2	1,2-Dichlorobenzene (ortho-)	600	0.1
n-Propylbenzene	--	0.2	1,2-Dichloroethane	5	0.2
Naphthalene	--	0.5	1,2-Dichloropropane	5	0.1
sec-Butylbenzene	--	0.2	1,3,5-Trimethylbenzene	--	0.2
Styrene	100	0.1	1,3-Dichlorobenzene	--	0.1
tert-Butylbenzene	--	0.2	1,3-Dichloropropane	--	0.2
Tetrachloroethylene	5	0.1	1,4-Dichlorobenzene (para-)	75	0.1
Tetrachloromethane (Carbon tet)	5	0.2	2,2-Dichloropropane	--	0.2
Toluene	1,000	0.2	2-Chlorotoluene	--	0.2
trans-1,2-Dichloroethylene	100	0.1	4-Chlorotoluene	--	0.2
trans-1,3-Dichloropropene	--	0.24	4-Isopropyl-1-methylbenzene	--	0.2
Tribromomethane (Bromoform)	*	0.2	--	--	--

## Laboratory Analyses

The current NWQL method for the analyses of VOCs is summarized in Rose and others (2016) and in references within. Samples are analyzed for ambient purgeable compounds to determine the suite of VOCs present (table 1). The NWQL verifies minimum detection limits or minimum reporting limits (MRL) for a rotating subset of analytes on a yearly

basis, if applicable (Foreman and others, 2021). The VOCs for which samples are analyzed by NWQL, the MRL for each compound, and maximum contaminant levels (MCLs) recommended by the U.S. Environmental Protection Agency (2020) are listed in table 1.

## Evaluation of Variability in Volatile Organic Compound Concentrations in Paired-Samples

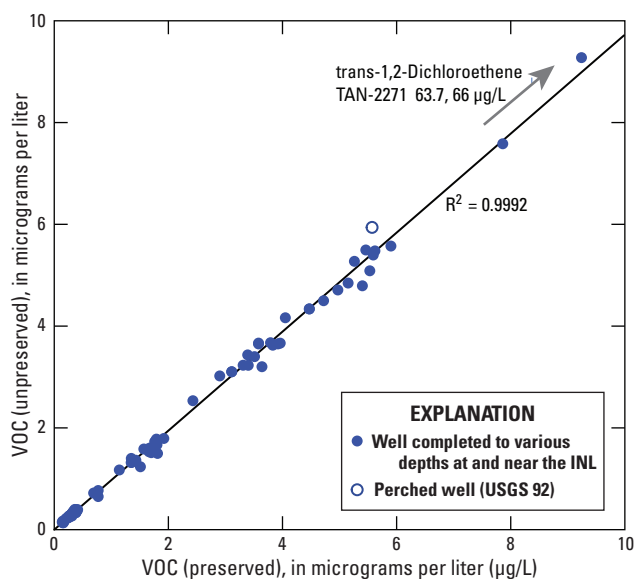
Results of the analyses of the water samples from selected wells at INL are presented in table 2. Eleven VOCs were detected in concentrations greater than the MRL of 0.1 or 0.2 µg/L in sample(s) from at least one well included in this study. Concentrations of most of the VOCs detected in the samples were below the MRLs, although concentrations greater than the MRL were detected in well USGS 92, completed in perched groundwater, and in wells at multiple depths within the eastern Snake River Plain aquifer (table 2). Detections above the MRL were in samples from 8 of the 11 wells at and near the RWMC, in samples from 2 of the 5 wells at and near the TAN area, and in samples from 1 well near the ATR Complex. Concentrations of tetrachloromethane (carbon tetrachloride) above the MCL were detected in samples from two wells at or near the RWMC: the RWMC production well and USGS 92. The concentration of trichloroethene was above the MCL in samples collected from USGS 92 and GIN-2.

Unpreserved samples showed no consistent bias for higher or lower concentrations than did preserved samples for VOCs at concentrations greater than their respective MRLs. For example, in all four unpreserved samples from well GIN-2 in which the concentrations of VOCs exceeded their respective MRLs, those concentrations were higher than the concentrations in the preserved paired-sample from that well. In samples from well M3S at RWMC, however, the concentrations of five VOCs that exceeded MRLs were lower in the unpreserved samples than in the preserved samples of each same sample-pair. Detections of VOCs in both preserved and unpreserved samples collected in this study are consistent, with respect to well locations and analytical results, with those in previous studies (Mairner and Bartholomay, 2016; Bartholomay and others, 2017; Bartholomay and others, 2020).

The variability in concentrations of VOCs from the analyses of paired-samples (unpreserved and preserved) were estimated by calculating the relative percent difference (*RPD*) between those concentrations. Uncertainties in analytical results are not provided, however, for the current NWQL laboratory methods for analyzing VOCs. Therefore, as an alternative measure of variability between concentrations of VOCs in the paired-samples, the normalized absolute difference (*NAD*) in the concentrations was calculated using pooled standard

deviation data for nearly all the VOCs measured for this study (Rose and others, 2016). Finally, to evaluate the difference between VOC concentrations in unpreserved and preserved sample pairs, a rank-sum test was performed for individual VOCs with greater than six paired-sample detections above their respective MRLs. Bias in the paired-samples was not directly measured but inferred from a qualitative review of quality-control (QC) samples collected in 2020, including field and source-solution blanks collected as part of the INLPO routine water-quality assurance program. The paired-samples stability of VOC concentrations is evaluated using *RPD* and (or) *NAD* (table 2), respectively.

A simple linear regression model of the predictor variable, or unpreserved sample, and the response variable, or preserved sample, shows that the data are highly correlated with an  $R^2$  of 0.9992 (fig. 3). This simple comparison of VOC concentrations in the paired-samples confirms that they are highly correlated and show a strong positive linear relation.



**Figure 3.** Simple linear regression of volatile organic compound concentrations in paired (unpreserved and preserved) samples from wells at the Idaho National Laboratory (INL), for concentrations greater than their respective minimum reporting levels.

**Table 2.** Concentrations of selected volatile organic compounds in water samples collected from multiple levels in selected wells, Idaho National Laboratory, Idaho, 2020.

[Data for this study can be found on the USGS National Water Information System at <http://dx.doi.org/10.5066/F7P55KJN>. Well name is the local well identifier used in this study, see [figs. 1, 2](#) for locations. Site Identifier is the unique well ID. Well Depth is the total depth of each well (ft). Constituent is the volatile organic compound (VOC) analyzed. Date refers to date sample collected on calendar month/day/year. Time refers to sample collection time in military time. Analytical results in micrograms per liter. Samples were analyzed at the U.S. Geological Survey National Water Quality Laboratory in Lakewood, Colorado for 61 volatile organic compounds; see [table 1](#) for compounds. Compounds not listed may have been present, but at concentrations below their reporting levels. **Abbreviations:** RPD, relative percent difference; NAD, normalized absolute difference; NA, not applicable; RL, reporting level; <, less than; standard deviation not available for cis-1,2-Dichloroethene; Chloroethane, trans-1,2-Dichloroethene, and 1,2-Dichloropropane]

Well name	Site identifier	Well depth	Constituent	Date	Time	Unpreserved	Time	Preserved	RPD	NAD
GIN-2	434949112413401	381	cis-1,2-Dichloroethene	10/20/2020	1357	0.126	1407	0.112	11.8	NA
			Tetrachloroethene			2.96		2.6	12.9	4.57
			Trichloroethene			9.62		9.15	5.01	1.18
			Trichloromethane			0.12		0.109	9.61	1.36
RWMC M3S	433008113021801	633	Tetrachloromethane	10/19/2020	1020	2.9	1030	3.02	4.05	0.96
			Trichloromethane			0.245		0.258	5.17	0.73
			Tetrachloroethene			0.156		0.164	5.00	1.77
			1,1,1-Trichloroethane			0.142		0.15	5.48	1.29
RWMC M7S	433023113014801	628	Trichloroethene	10/19/2020	1345	1.14	1355	1.17	2.6	0.61
			Tetrachloromethane			3.58		3.67	2.48	0.59
			Trichloromethane			0.694		0.72	3.68	0.52
			Tetrachloroethene			0.337		0.366	8.25	2.91
RWMC production well	433002113021701	685	1,1,1-Trichloroethane	1/15/2020	0944	0.264	0954	0.268	1.5	0.35
			Trichloroethene			2.43		2.53	4.03	0.95
			Tetrachloromethane			5.9		5.57	5.75	1.36
			Trichloromethane			1.92		1.79	7.01	0.99
RWMC production well	433002113021701	685	Tetrachloroethene	2/19/2020	0849	0.339	0859	0.337	0.59	0.21
			1,1,1-Trichloroethane			0.301		0.276	8.67	2.04
			Trichloroethene			3.92		3.65	7.13	1.68
			Tetrachloromethane			4.72		4.5	4.77	1.12
RWMC production well	433002113021701	685	Trichloromethane	2/19/2020	0849	1.66	0859	1.53	8.15	1.15
			Tetrachloroethene			0.362		0.357	1.39	0.49
			1,1,1-Trichloroethane			0.27		0.255	5.71	1.35
			Trichloroethene			3.79		3.67	3.22	0.76

**Table 2.** Concentrations of selected volatile organic compounds in water samples collected from multiple levels in selected wells, Idaho National Laboratory, Idaho, 2020. — Continued

[Data for this study can be found on the USGS National Water Information System at <http://dx.doi.org/10.5066/F7P55KJN>. Well name is the local well identifier used in this study, see [figs. 1, 2](#) for locations. Site Identifier is the unique well ID. Well Depth is the total depth of each well (ft). Constituent is the volatile organic compound (VOC) analyzed. Date refers to date sample collected on calendar month/day/year. Time refers to sample collection time in military time. Analytical results in micrograms per liter. Samples were analyzed at the U.S. Geological Survey National Water Quality Laboratory in Lakewood, Colorado for 61 volatile organic compounds; see [table 1](#) for compounds. Compounds not listed may have been present, but at concentrations below their reporting levels. **Abbreviations:** RPD, relative percent difference; NAD, normalized absolute difference; NA, not applicable; RL, reporting level; <, less than; standard deviation not available for cis-1,2-Dichloroethene; Chloroethane, trans-1,2-Dichloroethane, and 1,2-Dichloropropane]

Well name	Site identifier	Well depth	Constituent	Date	Time	Unpreserved	Time	Preserved	RPD	NAD
RWMC production well	433002113021701	685	Tetrachloromethane	3/16/2020	0845	5.4	0855	4.79	12.0	2.82
			Trichloromethane			1.7		1.51	11.8	1.67
			Tetrachloroethene			0.384		0.334	13.9	4.91
			1,1,1-Trichloroethane			0.309		0.268	14.2	3.34
			Trichloroethene			3.640		3.2	12.9	3.03
RWMC production well	433002113021701	685	Tetrachloromethane	4/13/2020	1036	5.46	1046	5.50	0.73	0.17
			Trichloromethane			1.8		1.77	1.68	0.24
			Tetrachloroethene			0.41		0.394	3.98	1.41
			1,1,1-Trichloroethane			0.313		0.321	2.52	0.59
			Trichloroethene			3.96		3.66	7.87	1.85
RWMC production well	433002113021701	685	Tetrachloromethane	5/11/2020	0858	5.53	0908	5.09	8.29	1.95
			Trichloromethane			1.8		1.67	7.49	1.06
			Tetrachloroethene			0.398		0.373	6.48	2.29
			1,1,1-Trichloroethane			0.325		0.3	8.0	1.88
			Trichloroethene			3.83		3.62	5.64	1.33
RWMC production well	433002113021701	685	Tetrachloromethane	6/15/2020	0907	5.59	0917	5.4	3.46	0.81
			Trichloromethane			1.76		1.73	1.72	0.24
			Tetrachloroethene			0.382		0.395	3.35	1.18
			1,1,1-Trichloroethane			0.287		0.289	0.69	0.16
			Trichloroethene			3.58		3.65	1.94	0.46
RWMC production well	433002113021701	685	Tetrachloromethane	7/15/2020	1015	5.26	1025	5.27	0.19	0.04
			Trichloromethane			1.57		1.58	0.63	0.09
			Tetrachloroethene			0.381		0.363	4.84	1.71
			1,1,1-Trichloroethane			0.265		0.266	0.38	0.09
			Trichloroethene			3.31		3.23	2.45	0.58

**Table 2.** Concentrations of selected volatile organic compounds in water samples collected from multiple levels in selected wells, Idaho National Laboratory, Idaho, 2020. — Continued

[Data for this study can be found on the USGS National Water Information System at <http://dx.doi.org/10.5066/F7P55KJN>. Well name is the local well identifier used in this study, see [figs. 1, 2](#) for locations. Site Identifier is the unique well ID. Well Depth is the total depth of each well (ft). Constituent is the volatile organic compound (VOC) analyzed. Date refers to date sample collected on calendar month/day/year. Time refers to sample collection time in military time. Analytical results in micrograms per liter. Samples were analyzed at the U.S. Geological Survey National Water Quality Laboratory in Lakewood, Colorado for 61 volatile organic compounds; see [table 1](#) for compounds. Compounds not listed may have been present, but at concentrations below their reporting levels. **Abbreviations:** RPD, relative percent difference; NAD, normalized absolute difference; NA, not applicable; RL, reporting level; <, less than; standard deviation not available for cis-1,2-Dichloroethene; Chloroethane, trans-1,2-Dichloroethene, and 1,2-Dichloropropane]

Well name	Site identifier	Well depth	Constituent	Date	Time	Unpreserved	Time	Preserved	RPD	NAD
RWMC production well	433002113021701	685	Tetrachloromethane	8/17/2020	0857	5.15	0907	4.85	6.0	1.41
			Trichloromethane			1.81		1.5	18.7	2.64
			Tetrachloroethene			0.38		0.338	11.7	4.13
			1,1,1-Trichloroethane			0.277		0.264	4.81	1.13
			Trichloroethene			3.4		3.23	5.13	1.21
RWMC production well	433002113021701	685	Tetrachloromethane	9/14/2020	0854	5.62	0904	5.48	2.52	0.59
			Trichloromethane			1.67		1.6	4.28	0.61
			Tetrachloroethene			0.331		0.346	4.43	1.57
			1,1,1-Trichloroethane			0.287		0.279	2.83	0.67
			Trichloroethene			3.39		3.43	1.17	0.28
RWMC production well	433002113021701	685	Tetrachloromethane	10/14/2020	1030	4.47	1040	4.34	2.95	0.70
			Trichloromethane			1.35		1.32	2.25	0.32
			Tetrachloroethene			0.308		0.309	0.32	0.11
			1,1,1-Trichloroethane			0.236		0.232	1.71	0.40
			Trichloroethene			3.11		3.1	0.32	0.80
RWMC production well	433002113021701	685	Tetrachloromethane	11/16/2020	1021	4.35	1031	4.36	0.23	0.05
			Trichloromethane			1.35		1.3	3.77	0.53
			Tetrachloroethene			0.308		0.309	0.32	0.11
			1,1,1-Trichloroethane			0.236		0.232	1.71	0.40
			Trichloroethene			3.11		3.1	0.32	0.80
RWMC production well	433002113021701	685	Tetrachloromethane	12/15/2020	0910	4.97	0920	4.71	5.37	1.27
			Trichloromethane			1.42		1.36	4.32	0.61
			Tetrachloroethene			0.378		0.368	2.68	0.95
			1,1,1-Trichloroethane			0.268		0.255	4.97	1.17
			Trichloroethene			3.51		3.4	3.18	0.75

**Table 2.** Concentrations of selected volatile organic compounds in water samples collected from multiple levels in selected wells, Idaho National Laboratory, Idaho, 2020. — Continued

[Data for this study can be found on the USGS National Water Information System at <http://dx.doi.org/10.5066/F7P55KJN>. Well name is the local well identifier used in this study, see [figs. 1, 2](#) for locations. Site Identifier is the unique well ID. Well Depth is the total depth of each well (ft). Constituent is the volatile organic compound (VOC) analyzed. Date refers to date sample collected on calendar month/day/year. Time refers to sample collection time in military time. Analytical results in micrograms per liter. Samples were analyzed at the U.S. Geological Survey National Water Quality Laboratory in Lakewood, Colorado for 61 volatile organic compounds; see [table 1](#) for compounds. Compounds not listed may have been present, but at concentrations below their reporting levels. **Abbreviations:** RPD, relative percent difference; NAD, normalized absolute difference; NA, not applicable; RL, reporting level; <, less than; standard deviation not available for cis-1,2-Dichloroethene; Chloroethane, trans-1,2-Dichloroethene, and 1,2-Dichloropropane]

Well name	Site identifier	Well depth	Constituent	Date	Time	Unpreserved	Time	Preserved	RPD	NAD
TAN 2271	435053112423101	280	1,1-Dichloroethane	11/12/2020	1015	0.279	1025	0.282	1.07	0.25
			Chloroethane			0.222		0.208	6.51	NA
			cis-1,2-Dichloroethene			0.648		0.577	11.59	NA
			Trichloroethene			1.51		1.58	4.53	1.07
			Vinyl chloride			0.664		0.714	7.26	1.03
			trans-1,2-Dichloroethene			63.7		66	3.55	NA
USGS 65	433447112574501	498	Trichloromethane	4/8/2020	1315	0.152	1325	0.168	10.0	1.41
USGS 87	433013113024201	673	Tetrachloromethane	4/8/2020	1128	4.05	1138	4.16	2.68	0.63
			Trichloromethane			0.380		0.384	1.05	0.15
			Tetrachloroethene			0.207		0.219	5.63	1.99
			1,1,1-Trichloroethane			0.167		0.161	3.66	0.86
			Trichloroethene			1.35		1.4	3.64	0.86
USGS 88	432940113030201	663	Tetrachloromethane	9/30/2020	1035	0.687	1045	0.599	13.69	3.22
			Trichloromethane			0.383		0.383	0	0
			Trichloroethene			0.550		0.493	10.93	2.57
USGS 92	433000113025301	214	Tetrachloromethane	4/13/2020	1203	5.57	1213	5.94	6.43	1.51
			Trichloromethane			9.24		9.28	0.43	0.06
			Tetrachloroethene			1.51		1.24	19.6	6.91
			1,1-Dichloroethane			0.154		0.135	13.1	3.09
			1,1,1-Trichloroethane			0.772		0.651	17.0	3.99
			1,2-Dichloropropane			0.158		0.136	15.0	NA
			Trichloroethene			7.86		7.58	3.63	0.85
USGS 120	432919113031501	705	Tetrachloromethane	10/14/2020	0905	1.79	0915	1.78	0.56	0.13
			Trichloromethane			0.361		0.398	9.75	1.38
			1,1,1-Trichloroethane			0.1		<0.1	NA	NA
			Trichloroethene			0.767		0.769	0.26	0.06
USGS 132	432906113025018	1238	Tetrachloromethane	6/15/2020	1326	0.372	1336	0.37	0.54	0.13

**Table 2.** Concentrations of selected volatile organic compounds in water samples collected from multiple levels in selected wells, Idaho National Laboratory, Idaho, 2020. — Continued

[Data for this study can be found on the USGS National Water Information System at <http://dx.doi.org/10.5066/F7P55KJN>. Well name is the local well identifier used in this study, see [figs. 1, 2](#) for locations. Site Identifier is the unique well ID. Well Depth is the total depth of each well (ft). Constituent is the volatile organic compound (VOC) analyzed. Date refers to date sample collected on calendar month/day/year. Time refers to sample collection time in military time. Analytical results in micrograms per liter. Samples were analyzed at the U.S. Geological Survey National Water Quality Laboratory in Lakewood, Colorado for 61 volatile organic compounds; see [table 1](#) for compounds. Compounds not listed may have been present, but at concentrations below their reporting levels. **Abbreviations:** RPD, relative percent difference; NAD, normalized absolute difference; NA, not applicable; RL, reporting level; <, less than; standard deviation not available for cis-1,2-Dichloroethene; Chloroethane, trans-1,2-Dichloroethene, and 1,2-Dichloropropane]

Well name	Site identifier	Well depth	Constituent	Date	Time	Unpreserved	Time	Preserved	RPD	NAD
CPP-1 <sup>1</sup>	433433112560201	586	NA	4/28/2020	0919	NA	0929	NA	NA	NA
Highway-3 <sup>1</sup>	433256113002501	750	NA	10/13/2020	1521	NA	1531	NA	NA	NA
No Name-1 <sup>1</sup>	435038112453401	550	NA	4/8/2020	1507	NA	1517	NA	NA	NA
TAN 2312 <sup>1</sup>	434939112422001	568	NA	10/19/2020	1403	NA	1413	NA	NA	NA
USGS 7 <sup>1</sup>	434915112443901	903	NA	4/8/2020	1318	NA	1328	NA	NA	NA
USGS 34 <sup>1</sup>	433334112565501	700	NA	4/20/2020	1210	NA	1220	NA	NA	NA
USGS 38 <sup>1</sup>	433322112564301	724	NA	4/20/2020	1323	NA	1333	NA	NA	NA
USGS 77 <sup>1</sup>	433315112560301	586	NA	4/17/2020	1205	NA	1215	NA	NA	NA
USGS 84 <sup>1</sup>	433356112574201	505	NA	10/19/2020	0943	NA	0953	NA	NA	NA
USGS 89 <sup>1</sup>	433005113032801	714	NA	4/8/2020	0943	NA	0953	NA	NA	NA
USGS 97 <sup>1</sup>	433807112551501	510	NA	4/27/2020	1213	NA	1223	NA	NA	NA
USGS 98 <sup>1</sup>	433657112563601	508	NA	10/19/2020	1208	NA	1218	NA	NA	NA
USGS 117 <sup>1</sup>	432955113025901	655	NA	10/20/2020	1030	NA	1040	NA	NA	NA
USGS 119 <sup>1</sup>	432945113023401	705	NA	4/28/2020	1149	NA	1159	NA	NA	NA
USGS 128 <sup>1</sup>	433250112565601	615	NA	10/20/2020	0840	NA	0850	NA	NA	NA

<sup>1</sup>All below reporting level

## Relative Percent Difference

The relative percent difference (*RPD*) is a direct measurement of the variability between two independent sets of data without considering analytical uncertainty. In this study, the datasets consisted of the concentrations of VOCs in a) unpreserved and b) preserved samples, respectively, of a co-located sample-pair. Only those sample-pairs in which VOCs were detected in both the unpreserved and the preserved samples from a well at concentrations above the MRL for each analyte were considered for evaluation ( $n = 100$ ). In one paired-sample set, that from well USGS 120, the concentration of 1,1,1-trichloroethane exceeded the MRL in the unpreserved sample but was less than the MRL in the preserved sample; thus, the data for this sample set were not included in the evaluation. A typical data-quality criterion, applied to this set of paired-sample data, is that equivalence is demonstrated when the *RPD* is equal to or less than 20 percent (Taylor, 1987).

*RPD* is calculated using formula (1);

$$RPD = \frac{ABS[x_1 + x_2]}{\left(\frac{x_1 + x_2}{2}\right)} * 100, \quad (1)$$

where

- RPD* is the relative percent difference,
- ABS* is the absolute value,
- $x_1$  is the concentration of a VOC for the unpreserved water sample, and
- $x_2$  is the concentration of a VOC for the preserved water sample.

Sample pairs with VOC concentrations greater than the MRL and with a calculated *RPD* of less than 20 percent were considered statistically equivalent. Of the samples in which VOC concentrations exceeded their respective MRL, the *RPDs* for all paired-samples evaluated ( $n = 100$ ) were less than 20 percent and thus are considered statistically equivalent (table 2).

## Normalized Absolute Difference

A second approach to test for variability, the normalized absolute difference (*NAD*), was applied to the concentrations of VOCs in the paired-samples that were detected above the MRL to determine if these values are statistically equivalent with the incorporation of analytical precision. When analytical uncertainties, or standard deviations, are not provided for the analytical method used by the laboratory, estimations of the standard deviations for individual analytes can be used for statistical comparison (Bartholomay and Williams, 1996). The standard deviations used to estimate the variability in concentrations of VOCs in groundwater are summarized in Rose and others (2016). The standard deviations for VOC concentrations were determined for different matrices including blank

source-water, surface water, and groundwater. The standard deviations for the VOC suite were determined from seven groundwater replicates, spiked at two concentrations, and preserved with HCl in the laboratory (table 14 in Rose and others, 2016). The standard deviation applied for each constituent detected at a concentration above the MRL (0.5 or 5 micrograms per liter) was chosen based on the value closest to the paired-sample concentrations being compared.

*NAD* is calculated using formula (2);

$$NAD = \frac{|x - y|}{\sqrt{(s_x)^2 + (s_y)^2}}, \quad (2)$$

where

- $x$  is the concentration of a VOC in the unpreserved water sample,
- $y$  is the concentration of a VOC in the preserved water sample,
- $s_x$  is the standard deviation for the concentration value closest to measured concentration, and
- $s_y$  is the standard deviation for the concentration value closest to measured concentration.

The paired-samples for each analyte detected at a concentration above the MRL were considered statistically equivalent at the 95-percent confidence level, or two standard deviations from the mean, if the  $NAD \leq 1.96$  (Volk, 1969). Given that this statistical test utilized estimated standard deviations (Rose and others, 2016), and the data are not normally distributed, the *NAD* equal or less than equal to 1.96 was used as a guide to test for equivalence (Rattray, 2012; Rattray, 2014). Based on this approach, 81 percent of the sample-pairs with VOC concentrations above the MRL are considered statistically equivalent using this statistical test for variability. The sample-pairs that were not considered statistically equivalent with the *NAD* method guidelines were those pairs that had the highest *RPD* (table 2). No bias was detected in the *NAD* results with respect to site locations, specific VOC constituents, or sample depth. While this approach to evaluate variability did not show the same level of statistical equivalence as the *RPD* approach, the *NAD* is used as a guide, given that the standard deviations are pooled and not specific to this suite of data. These results are consistent with those in the previous study by the USGS Office of Water Quality that evaluated the statistical equivalence of VOC concentrations and preservation technique on a wide range of sample types and VOC analytes (app. 1).

## Rank-Sum Test

To evaluate the equivalence between unpreserved and preserved samples in terms of concentrations of individual VOC's, the Mann-Whitney Wilcoxon rank-sum test was applied to analytical results from this study when concentration values above the MRL for an individual VOC were

**Table 3.** Summary of rank-sum statistical test results for individual volatile organic compound analytes.

[None of the paired-samples evaluated were statistically different]

Constituent	n (pairs)	p-value	Median difference
1,1,1-Trichloroethane	17	0.2033	0.0065
Tetrachloroethene	17	0.3209	0.021
Tetrachloromethane	19	0.2996	0.26
Trichloroethene	19	0.3254	0.16
Trichloromethane	20	0.3084	0.065

detected in more than six paired-samples (Helsel and others, 2020). Thus, the VOCs selected for further analysis included: 1,1,1-Trichloroethane, Tetrachloroethene, Tetrachloromethane, Trichloroethene, and Trichloromethane. The rank-sum test is a nonparametric test that evaluates the difference between two groups of data, the median difference between concentrations in VOCs in unpreserved and preserved samples. The null hypothesis ( $H_0$ ) is that the median of the difference of the concentrations are equal to zero, or that the number of negative differences is approximately the same as the positive differences between the concentrations in unpreserved and preserved paired-samples at a specified level of significance. The alternative hypothesis ( $H_A$ ) is that  $x > y$ , where  $x$  represents the unpreserved sample results and  $y$  represents the preserved sample results. This test, applied to the subset of data for individual VOCs, was applied with an  $\alpha$  of 0.90. The null hypothesis was rejected if the  $p$ -value was  $\leq 0.1$  (Helsel and others, 2020).

Mann-Whitney Wilcoxon Rank-Sum is calculated using formula (3);

$$H_0 : \text{median } [D_i] = 0; H_A : \text{median } [D_i] \neq 0, \quad (3)$$

where

- $x$  is the concentration of a VOC in the unpreserved water sample,
- $y$  is the concentration of a VOC in the preserved water sample, and
- $D_i$   $x_i - y_i$

This one-sided test was applied in the R environment using the “wilcox.test” function with the following parameters:  $x$  = unpreserved;  $y$  = preserved; alternative = “greater”; confidence level = 0.9 (R Core Team, 2019).

Results from the Mann-Whitney rank-sum (Wilcoxon) statistical test reveal that the medians of unpreserved and preserved VOC concentrations are not statistically different (table 3) even though the concentrations in the unpreserved samples were slightly higher than those in the preserved samples for all individual VOCs evaluated. The medians of the differences between the unpreserved and preserved VOC concentrations were less than 0.26  $\mu\text{g/L}$  for the subset of individual VOCs evaluated. These results give further confidence that there is no statistical difference in the concentrations of individual VOCs detected in laboratory analyses regardless of the sample preservation method used at time of sample collection. This subset of data accounts for 92 percent of all VOC concentrations above the MRL measured for this study.

## Bias

As a general practice, the potential for the introduction of environmental bias during groundwater sampling at the INL is periodically evaluated on the basis of analyses of quality-control (QC) samples collected during the collection of environmental samples. These QC samples include equipment, field, and source-solution blank samples, as appropriate. During all routine water-quality sampling at the INL in 2020, QC samples were collected to validate field-sample collection practices and protocols. Although in 2020 the QC samples were not collected and analyzed specifically for VOCs, an analysis of QC samples collected during previous periods of sampling specifically for VOCs from 1996 through 2018 (Rattray, 2012, 2014; Davis and others, 2013; Bartholomay and others, 2017, 2020) did not show any potential bias, field-equipment, or source-solution blank contribution that would indicate any bias introduced by field-collection techniques, sample preservation, or sample handling. This study did not evaluate the effects of the collection and preservation of “spiked” QC samples on the results of the analyses of those samples for VOCs. A “spiked” sample is prepared in a laboratory with a known concentration of an analyte to evaluate any potential sample preparation and analysis method bias at the laboratory. There is no consistent positive or negative bias to VOC concentration data determined for this suite of paired-samples from either preservation method.

## Summary

During 2020, water samples were collected from 25 wells completed in the eastern Snake River Plain aquifer and 1 well completed in perched groundwater above the aquifer at the Idaho National Laboratory as part of the U.S. Geological Survey's quality-assurance program to determine the effect of different sample preservation methods on the laboratory-determined concentrations of volatile organic compounds (VOCs). One of two samples (a paired-sample set) collected sequentially at each well was preserved with hydrochloric acid; the other sample was not acidified. Both samples were chilled after collection and during shipment to the USGS National Water Quality Laboratory, where they were analyzed for 61 VOCs.

Statistical analyses of the analytical results—the concentrations of VOCs in the samples, support a conclusion that the field-sample collection and preservation method did not result in measurable, or statistically significant, variability in the concentration of VOCs in the paired-samples. The percentage of paired-samples with acceptable reproducibility was 100 percent for all detectable VOCs at concentrations above the Minimum Reporting Level (MRL), as evidenced by the relative percent difference (*RPD*) statistical comparison. When estimated uncertainty is included in the evaluation, approximately 81 percent of the samples are statistically equivalent when the normalized absolute difference (*NAD*) is used as a statistical guide. Comparing the concentrations of individual VOCs greater than the MRL in at least six sets of paired-samples using the Mann-Whitney rank-sum statistical test showed no statistical difference between the paired-samples.

Comparability between past, current, and future analytical results supports a robust and defensible VOC-monitoring network at the INL. The findings of this study provide evidence that any slight variability in laboratory-determined concentrations of chemical constituents that may result from differences in the sample preservation method will not compromise comparisons of historical and current VOC data or with long-term geochemical evaluations.

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## Appendix 1. U.S. Geological Survey Water Quality Memorandum, January 30, 1996

This appendix contains a 1996 memorandum released for internal use in the U.S. Geological Survey Water Resources Division, which has since been renamed the Water Resource Mission Area. The memorandum was created for internal dissemination and was not peer-reviewed. It is presented here to provide record of data cited in this report.

Water Resources Division  
South Dakota District Office  
1608 Mountain View Road  
Rapid City, SD 57702

January 30, 1996

### Memorandum

To: Dave Rickert and Pete Rogerson  
From: Joyce E. Williamson and Gregory C. Delzer  
Subject: Results comparing VOC concentrations in samples preserved with HCl + 4° chill versus 4° chill only

### INTRODUCTION

In the past, most volatile organic chemical (VOC) samples sent to the National Water-Quality Laboratory (NWQL) were chilled to 4°C without additional preservation. VOC samples analyzed by the NWQL are currently preserved in the field with 1:1 HCl and chilled to 4°C. The goal of this study was to document the effect of the standard operating procedure (SOP) change using HCl plus 4°C chill (hereafter referred to as "HCl" samples) as a VOC preservation agent in lieu of 4°C chill only (hereafter referred to as "no HCl" samples).

### DESIGN

This study incorporated 13 sampling sites from a variety of settings and water types. Of these 13 sites, six were ground waters, three were surface waters, two were stormwaters, and two were sewage effluents (appendix 1). The sample preparation sequence and description of sample types collected at each site are listed in table 1. All samples were held for 14 days and analyzed at the NWQL in a random and sequential order. Statistical comparisons between HCl samples and no HCl samples were used to document the effect of the SOP change. Analytical results for the environmental samples, lab spikes, and DIW spikes are not presented herein but are contained in a South Dakota District data base. Additional information on these data and the sampling sites are available from Joyce Williamson or Greg Delzer.

Table 1. --Sample preparation sequence, type, and number of samples (N), and the type of preservation for each sample type

Sample Sequence	Sample Type	N	Type of Preservation
1	native water	3	Ascorbic acid, 2 drops of 1:1 HCl, 4° chill
2	HCl preserved + 4° chill	2	Ascorbic acid, 2 drops of 1:1 HCl, spike 5 ug/L, 4° chill (HCl samples)
3	4° chill only	2	4° chill (no HCl samples), spike 5 ug/L

**Figure 1.1.** This figure is a digital copy of a U.S. Geological Survey memorandum circulated internally on January 30, 1996. The memorandum was not peer-reviewed and was released in the U.S. Geological Survey Water Resources Division, which has since been renamed the Water Resource Mission Area. The memorandum can be accessed at <https://doi.org/10.3133/sir20225076>.



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