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

Prepared in cooperation with
Idaho Soil Conservation Commission

Soil Analyses for 1,3-Dichloropropene (1,3-DCP), Sodium N-Methyldithiocarbamate (Metam-Sodium), and Their Degradation Products Near Fort Hall, Idaho, September 1999 Through March 2000

Water-Resources Investigations Report 01–4052

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Cover photo: Soil sample collection, October 1999; personnel from the Natural Resources Conservation Service (NRCS) and Idaho Soil Conservation Commission

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By D.J. Parliman

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Boise, Idaho
2001

U.S. DEPARTMENT OF THE INTERIOR
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U.S. GEOLOGICAL SURVEY
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CONVERSION FACTORS, VERTICAL DATUM, AND OTHER ABBREVIATED UNITS

Multiply	By	To obtain
foot (ft)	0.3048	meter
inch (in.)	2.54	centimeter
mile (mi)	1.609	kilometer

Temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8)\,(°C)+32$$

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Other abbreviated units:

cc	cubic centimeter, multiply by 0.06102 to obtain cubic inch
g	gram, multiply by 0.0353 to obtain ounce
µg/L	microgram per liter, equal to parts per billion
mg/L	milligram per liter, equal to parts per million
mL	milliliter

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ABSTRACT

Between September 1999 and March 2000, soil samples from the Fort Hall, Idaho, area were analyzed for two soil fumigants, 1,3-dichloropropene (1,3-DCP) and sodium n-methyldithiocarbamate (metam-sodium), and their degradation products. Ground water is the only source of drinking water at Fort Hall, and the purpose of the investigation was to determine potential risk of ground-water contamination from persistence and movement of these pesticides in cropland soils.

1,3-DCP, metam-sodium, or their degradation products were detected in 42 of 104 soil samples. The samples were collected from 1-, 2-, and 3-foot depths in multiple backhoe trenches during four sampling events—before pesticide application in September; after application in October; before soil freeze in December; and after soil thaw in March. In most cases, concentrations of the pesticide compounds were at or near their laboratory minimum reporting limits.

U.S. Environmental Protection Agency Method 5035 was used as the guideline for soil sample preparation and analyses, and either sodium bisulfate (NaHSO4), an acidic preservative, or pesticide-free water was added to samples prior to analyses. Addition of NaHSO4 to the samples resulted in a greater number of compound detections, but pesticide-free water was added to most samples to avoid the strong reactions of soil carbonate minerals with the NaHSO4. As a result, nondetection of compounds in samples containing pesticide-free water did not necessarily indicate that the compounds were absent.

Detections of these compounds were inconsistent among trenches with similar soil characteristics and histories of soil fumigant use. Compounds were detected at different depths and different trench locations during each sampling event.

Overall results of this study showed that the original compounds or their degradation products can persist in soil 6 months or more after their application and are present to at least 3 feet below land surface in some areas.

A few of the soil analyses results were unexpected. Degradation products of metam-sodium were detected in samples from croplands with a history of 1,3-DCP applications only, and were not detected in samples from croplands with a history of metam-sodium applications. Although 1,2-dibromoethane (EDB) has not been used in the area for many years, EDB was detected in a few soil samples. The presence of EDB in soil could be caused by irrigation of croplands with EDB-contaminated ground water.

Analyses of these soil samples resulted in many unanswered questions, and further studies are needed. One potential study to determine vertical extent of pesticide compound migration in sediments, for example, would include analysis of one or more columns of soil and sediments (land surface to ground water, about 35 to 50 feet below land surface) in areas with known soil contamination. Another study would expand the scope of soil contamination to include broader types of cropland conditions and compound analyses.

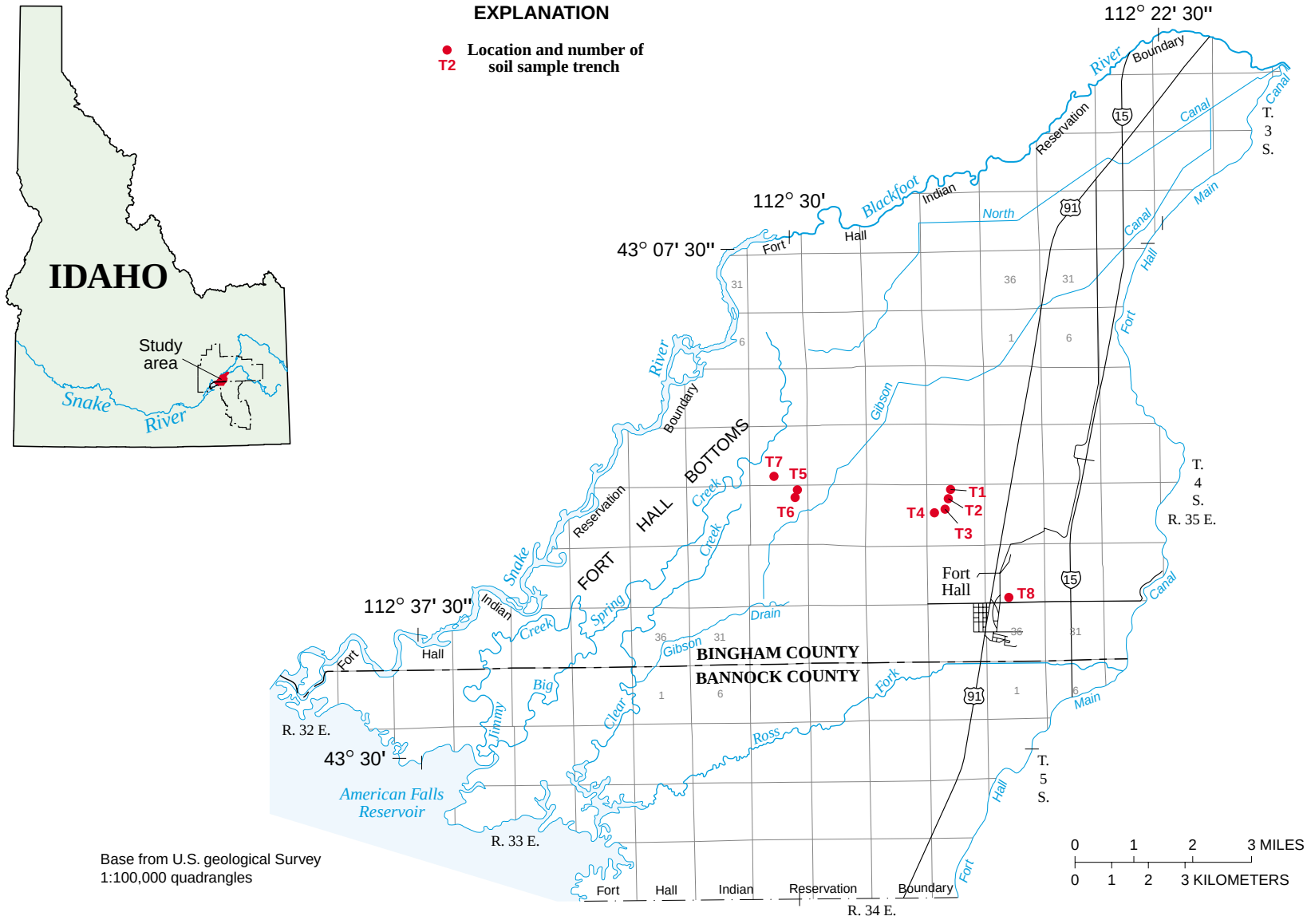

Figure 1. Location of Fort Hall, Idaho, and soil sample trenches.

INTRODUCTION

In 1999, the U.S. Geological Survey (USGS), in cooperation with the Idaho Soil Conservation Commission (representing the Shoshone-Bannock Tribes), began a study to monitor movement of two soil fumigants—1,3-dichloropropene (1,3-DCP) and sodium n-methyldithiocarbamate (metam-sodium)—through the soil profile (root zone) in areas near Fort Hall, Idaho (fig. 1). Ground water is the only source of drinking water in this area. Ground-water contaminants[1] in this area include concentrations of nitrate and 1,2-dibromoethane (ethylene dibromide or EDB) that exceed the U.S. Environmental Protection Agency (EPA) public drinking-water limits of 10 mg/L (as nitrogen) and 5 µg/L, respectively (U.S. Environmental Protection Agency, 2000). Relatively small concentrations of several other volatile organic compounds (VOCs) and pesticides also are present in ground water in the area (Parliman and Young, 1993; USGS Idaho District water-quality data base; L. DeJongh, Shoshone-Bannock Tribes, written commun., 1995). Soil fumigants have been used extensively on Fort Hall area croplands, and personnel with agricultural agencies and the Shoshone-Bannock Tribes have been increasingly concerned about potential movement of additional contaminants, including soil fumigation compounds, to ground-water zones.

[1]Contaminants are components that can limit water suitability for use or can represent degradation of water quality.

Purpose and Scope

The purpose of this report is to describe approaches, methods, and results of a study to determine potential risk of ground-water contamination from use of 1,3-DCP and metam-sodium (soil fumigants) in areas near Fort Hall, Idaho. Existing soil-sampling procedures were used or adapted to collect samples representative of 1- to 3-ft soil depths. Samples periodically were collected from several cropland locations to determine persistence and migration of fumigant compounds moving through the soil zone. Suggestions were proposed for further study of the vertical extent and transport mechanisms of these compounds to help determine their potential movement to ground-water zones.

Description of Study Area

Soil sample areas were located in irrigated croplands near Fort Hall in southeastern Idaho (fig. 1). The land surface is gently undulating, and land surface elevation is about 4,430 ft above sea level. Economy of the area is strongly influenced by irrigated agriculture. Major crops include potatoes, grains, and alfalfa. Crops are irrigated from about mid-April through September. Irrigation water is provided by surface-water diversions (canals and ditches) and numerous, large-capacity wells.

The climate is semiarid, characterized by cold, wet winters and hot, dry summers. Mean annual precipitation from August 1948 through July 2000 was 11.33 in. (National Weather Service, accessed October 25, 2000, online); precipitation generally is greatest during winter and spring and least during late summer. Average total monthly precipitation (September 1948 through March 2000) and total monthly precipitation for September 1999 through March 2000 are shown in table 1.

Weather conditions in the study area were unusually dry in late 1999 and unusually wet during early 2000. Total cumulative precipitation during September, October, November, and December 1999 (0.79 in.) was about 22 percent of normal (3.54 in.), and ground-water irrigation of fields continued into late October,

Table 1. Selected precipitation records for Fort Hall, Idaho

Precipitation (inches)	September	October	November	December	January	February	March
Average total monthly, 9/1/1948 to 3/31/2000	0.79	0.91	0.96	0.88	0.93	0.83	0.98
Total monthly, 9/1/1999 to 3/31/2000	0.02	0.39	0.11	0.27	1.45	1.50	0.81

several weeks longer than usual (J. Helsel, Shoshone-Bannock Tribes, oral commun., October 2000). Total cumulative precipitation during January, February, and March (3.76 in.) was about 137 percent of normal (2.74 in.). Soil freeze occurred after the December 1999 sampling event, and soil thaw occurred in about mid-February 2000.

Principal rock units in the study area are recent, unconsolidated stream and windblown deposits; older stream, glacial, windblown, lake, and playa deposits; and basalt and associated interbeds. Unconsolidated gravel, sand, silt, and clay are the predominant deposits and overlie the basalt (Parliman and Young, 1993, p. 4). Generalized soil characteristics for areas near sampling trenches are shown in table 2.

Soil Fumigants

Soil fumigants are chemicals (pesticides) that form gases that diffuse through soil. Fumigants such as 1,3-DCP and metam-sodium are volatile liquids, existing as liquids under normal temperatures and pressures but vaporizing after injection into soil. Effectiveness of soil fumigation depends on environmental factors (soil moisture, temperature, texture, amount of organic matter, and compaction, for example) that change pore space characteristics in soil or solubility of fumigants in soil and water.

Table 2. Generalized characteristics of soils near sampling trenches, Fort Hall, Idaho

[T, trench number; locations shown in figure 1]

T1, T2, T3, and T4	Sheepskin-Magallon Variant-Bartonflat Variant complex and Kukvey loamy sand, 0 to 3 percent slope: Mixed coarse and gravelly or sandy alluvium, including gravelly loamy sand; sandy loam; and calcareous sand.
T5 and T6	Paniogue Variant-Tickason complex, 0 to 2 percent slope: Mixed loamy alluvium overlying sands and gravel, including loam; silty, calcareous, or cobbly loam; sand; and gravelly sand.
T7	Bahem silt loam, 0 to 2 percent slope: Mixed silty alluvium overlying sand and gravel, including silt loam, gravelly loamy sand, and sand.
T8	Tickason sandy loam, 0 to 2 percent slope: Mixed alluvium including loam and sandy, silty, gravelly, or calcareous loam.

1,3-DCP and metam-sodium commonly are used in the Fort Hall area for preplanting soil treatment. These chemicals are general soil biocides (fungicide, herbicide, and nematocide) and often are applied to cropland by injection into soil to about 18 in. (1,3-DCP) or through irrigation systems (metam-sodium). Many published, unpublished, and Internet-accessible documents are available on the general topic of soil fumigants, and inconsistencies in information exist, including levels of toxicity to humans and environmental fate and effects of parent compounds and degradation products. General information on 1,3-DCP and metam-sodium presented in table 3 is compiled from sources listed in the Selected References section.

Data on degradation rates, solubility, leachability rank, and risks of human exposure are not included in table 3 because these factors are strongly influenced by changing environmental factors in the soil or because a wide range of reported study results are available. In general, parent products are reported to degrade moderately rapidly (several weeks) to rapidly (hours), and degradation products can be of more concern than the parent product to human health. For example, metam-sodium is a minimal human health hazard, but the degradation products methyl isothiocyanate (MITC) and hydrogen sulfide are moderately to strongly poisonous.

Formulations of these pesticide products have changed over time and vary among manufacturers, but commercial formulations of 1,3-DCP currently (2000) contain an approximately 50:50 mixture of *cis*- and *trans*- isomers (compounds that have the same molecular formula but different molecular structures). Isomers of 1,3-DCP degradation products also are listed in table 3.

Detection of Soil Fumigant Compounds in Ground Water

Ground water from the Fort Hall area has been analyzed for VOCs, including 1,3-DCP degradation compounds and commercial product contaminants, for more than 10 years as part of a statewide ground-water quality monitoring program and by the Shoshone-

Table 3. Selected information on 1,3-dichloropropene (1,3-DCP) and sodium n-methyldithiocarbamate (metam-sodium)

[CAS RN, Chemical Abstract Service Registry Number; URL, Uniform Resource Locater, a protocol for specifying addresses on the Internet; MSDS, Material Safety Data Sheet]

Chemical Name:	1,3-dichloropropene (CAS RN 542-75-6)
Synonym:	1,3-DCP or 1,3-D
Chemical formula:	C3H4Cl2
Isomers:	*cis*- and *trans*-1,3-dichloropropene
Degradates include:	*cis*- and *trans*-3-chloroallyl alcohol (CAAL) *cis*- and *trans*-3-chloroacrylic acid (CAAC) carbon dioxide (CO2)
Application practices:	generally injected into soil
URL for MSDS :	http://www.horizononline.com/MSDS_Sheets/992.txt
Other ingredients or contaminants included in current or previous commercial products:	1,3,3-trichloropropene (1,3,3-TCP) 1,2-dichloropropane (1,2-DCP) 1,3-dichloropropane (1,3-DCP) 1,2,3-trichloropropane (1,2,3-TCP) 1,2,2-trichloropropane (1,2,2-TCP) 1,1,2-trichloroethane (1,1,2-TCE) epichlorohydrin (EPI)
Chemical Name:	sodium n-methyldithiocarbamate (CAS RN 137-42-8)
Synonym:	metam-sodium or metham-sodium
Chemical formula:	C2H4NNaS2
Isomers:	none
Degradates include:	methyl isothiocyanate (MITC) n,n-dimethyl thiuram disulfide carbon disulfide (CS2) hydrogen sulfide (H2S) monomethylamine nitrogen oxides sulfur (at pH 9.5)
Application practices:	injected into soil or applied through irrigation system
URL for MSDS:	http://www.barc.usda.gov/fmod/sohes/msds_lab.htm
Other ingredients or contaminants included in current or previous commercial products	information not available

Bannock Tribes. To date, these compounds have not been detected in water analyses for the two programs.

A trace amount of 3-chloroacrylic acid, a degradation product of 1,3-DCP, is reported to have been detected in ground water from a well near Fort Hall as part of an ongoing, nationwide tapwater study related to re-registration of a commercial brand of soil fumigant (I. VanWesenbeeck, Dow Agrosciences, written commun., December 2000). The tapwater study currently is not complete and results have not been published. There is no EPA public drinking-water limit for 3-chloroacrylic acid (U.S. Environmental Protection Agency, 2000).

Acknowledgments

Successful completion of all phases of this project required the experience, expertise, and cooperation of many people from numerous agencies and groups. Special thanks are given to Jim Wood, Idaho Soil Conservation Commission (Boise); Wayne Duffy, Natural Resources Conservation Service (NRCS-Boise); John Helsel, Shoshone-Bannock Tribes (Fort Hall); LaGrande Coby, Shoshone-Bannock Tribes (Fort Hall); Michael Hepworth, Idaho Department of Agriculture (Idaho Falls); Steve Riedy, Idaho Department of Agriculture (Pocatello); Brad Duncan (NRCS-Idaho Falls); Jim Baker, Idaho Department of Agriculture (Boise); John Taberna, Western Agricultural Research (Blackfoot); and landowners near Fort Hall for access to their fields. Thanks also are extended to Ian VanWesenbeeck, Dow Agrosciences (Indianapolis) for information on DowElanco studies of the fate of 1,3-DCP in soils (Knuetson and others, 1997; Douglas and others, 1998; Kennard and Buehrer, 1998) and for providing the USGS National Water Quality Laboratory (NWQL) with standards for selected compounds.

STUDY APPROACHES

From July to September 1999, study approaches were developed, including consideration of questions about collection and analyses of whole soil versus soil gas samples, potential cross contamination of soil zones by hole construction methods and sample container placement/retrieval, and concerns for health and safety during soil sampling. Passive soil gas sampling (described by Vroblesky and others, 1996, p. 225–226; and Vroblesky and Robertson, 1996, p. 198-199) and active soil gas sampling (by probe and onsite gas chromatograph analysis) were considered but not used. For this study, whole soil samples were collected to increase possibilities of detecting small amounts of pesticide compounds and to avoid some disadvantages in soil gas sampling. Disadvantages for passive sampling were the increased labor and time required to place and retrieve soil gas equipment; compression and disturbance of soil to place and retrieve equipment that might affect compound detection; and potential health hazards to personnel when placing and retrieving equipment. Disadvantages for active soil gas sampling primarily were increased costs for labor and equipment and concern for potential onsite health hazards to personnel.

A truck-mounted auger was tested for possible use in soil sample collection, but auger drilling was impeded by cobble zones in the soil. The most cost-effective, labor- and time-efficient method with the least number of soil-compaction, soil-disturbance, and health-hazard problems for personnel was use of a backhoe to dig shallow sampling trenches. The backhoe and backhoe operator were supplied by the Shoshone-Bannock Tribes (fig. 2).

In September 1999, personnel from the Shoshone-Bannock Tribes Agricultural Resources office and the NRCS (Idaho Falls) chose locations for soil sample collection. Choices for locations were based primarily on history of pesticide and cropland uses, variety of soil types, accessibility during fall and winter months, and landowner permission. Initially, four areas were

Figure 2. Backhoe constructing a soil sampling trench, October 1999, Fort Hall, Idaho.

chosen for soil sample collection—three areas with greater than 5 years of 1,3-DCP use only and one area with metam-sodium use only. Soil samples were collected from seven backhoe trenches in the four areas—five trenches (T1, T2, T5, T6, and T7) in 1,3-DCP-only areas and two trenches (T3 and T4) in the metam-sodium-only area (fig. 1). In each trench, soil samples were collected from 1-, 2-, and 3-ft depths below land surface.

Soil samples were collected four times between September 1999 and March 2000. The sampling dates were chosen to represent soil conditions prior to application of pesticides (September), immediately after pesticide application (early October), before soil freeze and after fall rain events (December), and after soil thaw (March). The first sampling event was September 8, 1999. The second sampling event was October 19, 1999, at least 2 weeks after fumigants were applied. In October, metam-sodium was applied to previously 1,3-DCP-only areas (T5, T6, and T7), and T5 was replaced with T8, located in an area with at least 5 years of 1,3-DCP-only use (fig. 1).

The third sampling was completed on December 7, 1999, at least 6 weeks after the irrigation wells were shut down and irrigation ditches were dry. The fourth and final sampling was March 23, 2000, approximately 1 month after soil thaw in the area but before spring irrigation or cropland preparation.

SAMPLING PROCEDURES AND METHODS

EPA Method 5035 (U.S. Environmental Protection Agency, 1996) was used as the basis for onsite procedures and methods. Excerpts from EPA Method 5035, including Section 6—Sample collection, preservation, and handling—are provided in appendix A. Soil and quality assurance samples were analyzed at the NWQL in Denver, Colorado, and a USGS memorandum describing the custom method developed for analyses of the whole soil samples is provided in appendix B.

Some existing sampling methods were adapted or new methods developed to address concerns for minimizing soil disturbance; potential sample contamination from onsite techniques; cross contamination of soil sampling sites within each trench and from one trench to another; consistency of procedures among sampling sites, trenches, and dates; reactivity of soil to sodium bisulfate ($NaHSO_4$) preservative; personnel safety during sampling; and cost factors. Onsite procedures and methods can be separated into three parts—sampling preparations, soil sample collection, and sample processing.

Sampling Preparations

USGS personnel completed all sampling preparations. Tare weights, to 0.01 g, were recorded for each 40-mL glass sample bottle (including magnetic stir bar, 5 mL $NaHSO_4$ preservative or 5 mL pesticide-free water, label, septum cap, and dust cap). Bottles containing $NaHSO_4$ were prepared commercially. Bottles containing pesticide-free water were prepared at the USGS Idaho District laboratory in Boise, Idaho.

Sets of supplies were prepackaged (ziplock bags) for each sample site. Each package included two 40-mL, tare-weight sample bottles and one 40-mL empty bottle; stainless steel sampling scoop; and one 12-cc safety syringe with end plug removed and safety tube covered with aluminum foil (fig. 3). Extra sets of bottles were included for replicate samples.

Soil Sample Collection

A team of personnel from the USGS, Idaho Soil Conservation Commission, NRCS, Shoshone-Bannock Tribes, Idaho Department of Agriculture, and Western Agricultural Research collected the soil samples. The backhoe blade was cleaned with a hot-water,

Figure 3. A set of soil sampling supplies.

Figure 4. Backhoe blade being cleaned with a hot-water, high-pressure sprayer, October 1999, Fort Hall, Idaho

high-pressure sprayer before each trench was dug (fig. 4). Trenches were dug to a depth of about 3.5 to 4 ft; the face at the front edge of the trench was relatively vertical (fig. 5). Global Positioning System (GPS) measurements were made at trench sites to document locations of the trenches. Trenches were constructed in approximately the same areas as for earlier sampling events (but not the same locations) in an effort to duplicate soil conditions while avoiding use of previously disturbed soil.

A pocket tape was used to measure 1-, 2-, and 3-ft depths from land surface. Sampling began at the 3-ft depth and successively proceeded to 2-ft and 1-ft depths to prevent cross contamination of soil samples within the trench. At each depth, a stainless steel trowel was used to scrape approximately 1 in. of soil away

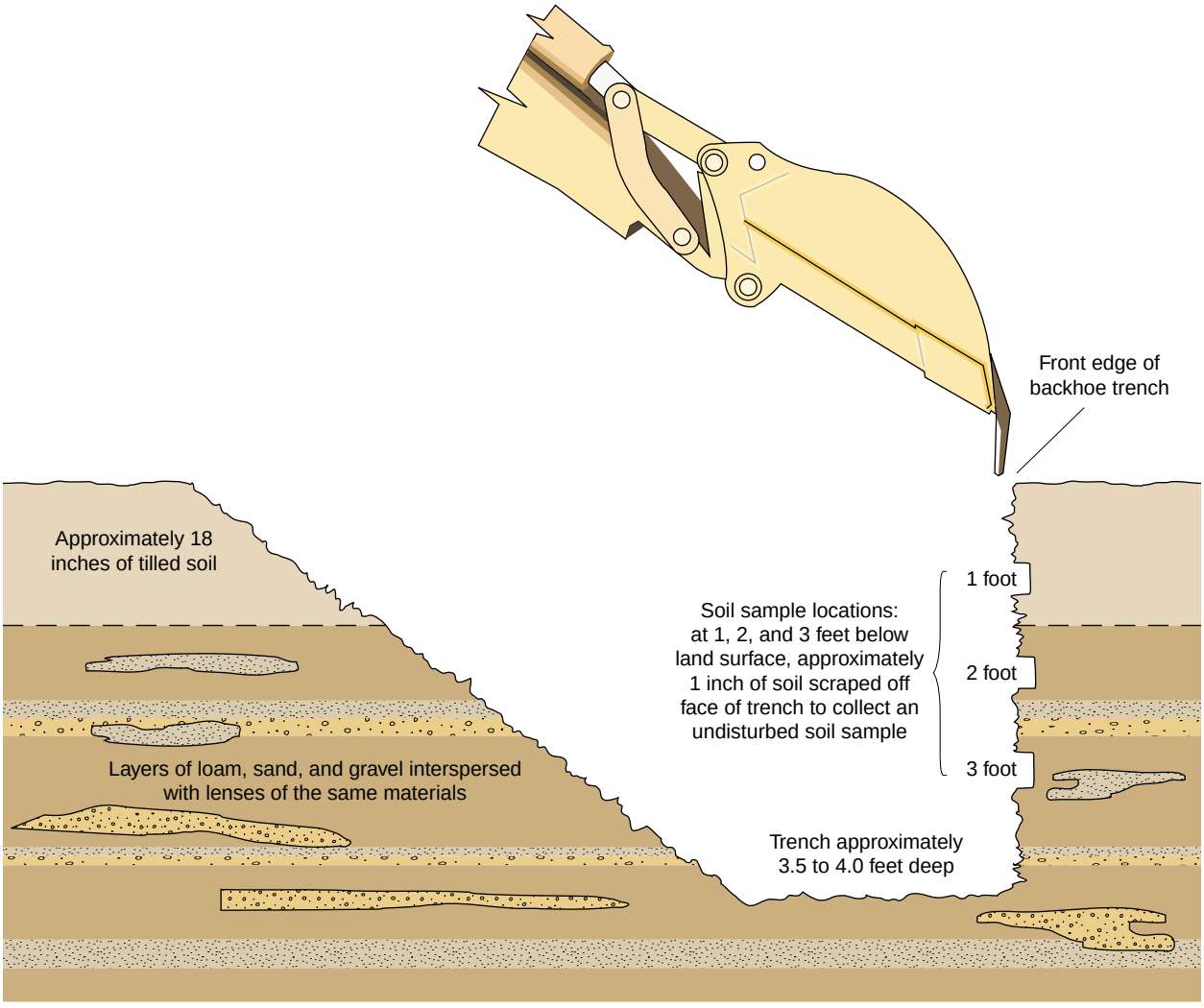

Figure 5. Generalized diagram of a soil sampling trench.

from the trench face and expose uncompressed soil that had not come in contact with the backhoe blade. Personnel collected soil samples in the shield section of a safety syringe by pushing the shield into the freshly exposed soil or by scooping soil into the shield with a stainless steel scoop when the soil zone was cobbly or densely packed (usually from silt or clay content). When the syringe shield was full, aluminum foil was placed over the top and the covered sample was placed into the syringe casing (fig. 3). An empty, 40-mL bottle also was filled with soil sample for laboratory soil moisture analyses.

After the soil sample was collected, sampling syringes, soil moisture bottle, and sample scoop were placed in a ziplock bag labeled with sampling site location, and the ziplock bag was placed in an ice chest. The stainless steel trowel was scrubbed with a detergent solution and rinsed with deionized water before 2-ft and 1-ft zones within each trench were sampled.

Latex or nitrile gloves were worn by all personnel collecting or handling soil samples at each site. During the October sampling, personnel in the trench collecting soil samples and an observer at land surface were required to have enclosed-space, hazardous materials training and to wear appropriate respiratory equipment and protective clothing (cover photo). Although samples were collected several weeks after soil fumigant application and at least a week beyond required area-entry restrictions, there was a possibility that toxic or hazardous fumes may have persisted in some soil zones in the trench. During December and March sampling, protective clothing continued to be worn in the trench to keep potentially contaminated soil from contacting clothing or skin.

Sample Processing

Collection of samples from all trenches on each sampling date required about 2 hours, and when sampling was complete, each sample set was prepared for shipment and laboratory analyses. Samples were prepared at or near a sampling location by USGS personnel.

Soil samples were prepared in order from earliest to latest collection time. Tare-weight bottles containing 5 mL of NaHSO4 or pesticide-free water were placed on a portable electronic scale, and the weight was zeroed. The aluminum cover on the syringe shield was removed, about 1/4 to 1/2 in. of soil was pushed up from the shield and discarded, and about 5 g (±0.5 g) of the remaining soil was extruded or scooped out and transferred to the prepared sample bottle. The bottle was recapped with the septum cap and dust cover; then site, sampling information, and total sample weight were written on the bottle label.

After two sample bottles and one soil moisture bottle were prepared for each sampling site, bottles were put in a foam shipping container, which was placed in a large ziplock bag, and the bag was placed in an ice chest. Ice was double-bagged in ziplock bags to ensure that ice water did not come in contact with sample bottles. Sample sets were shipped to the NWQL within about 24 hours of sample collection. Samples arrived at the laboratory within about 48 hours of sample collection.

Weighing paper was used during onsite sample weighing to keep the scale pan clean and avoid cross contamination of sample bottle sets. Powder-free latex gloves were worn at all times, and the sample preparation area was cleaned between sample sets. Used, disposable equipment and supplies were sealed in plastic bags and put in solid waste collection bins. Excess soil was left at the sample processing site.

Sodium bisulfate is an acidic preservative added to soil samples except “when samples are known or suspected to contain high levels of carbonates” (U.S. Environmental Protection Agency, 1996). Before the samples collected in September 1999 were transferred to bottles containing NaHSO4, dilute hydrochloric acid was added to small amounts of the soil sample to check for carbonate content. Many soil samples strongly effervesced and most samples moderately effervesced when the acid was added. Pesticide-free water, an alternative approach for sample preparation described in Method 5035, was not available during soil sample preparation in September, and soil samples with the strongest reaction to acid were sent to the laboratory in bottles containing only stir bars. Samples with small or moderate reaction to acid were sent with NaHSO4 preservative added. At the laboratory, 5 mL of pesticide-free water was added to dry samples.

Pesticide-free water was added to most soil sample sets collected in October and December 1999 and March 2000 to establish sample preparation continuity between sampling events and to reduce possibilities of strong chemical reactions in sample bottles. A few replicate samples with NaHSO4 preservative added were sent to the laboratory along with the October and March sample sets for analyses comparisons. Selection

of sampling sites for addition of NaHSO4 to replicates was based, in part, on previous detections of pesticide compounds with NaHSO4 preservative and history of reactivity of soil to the preservative. After September, all samples were sent to the laboratory either with water or NaHSO4 solutions.

About three replicate sets of soil samples were collected on each sampling date for quality control/quality assurance. Pesticide-free water only was added to most replicate samples, but at some locations, both water and NaHSO4 were added to replicates. Most locations for replicate collection were randomly selected. A few replicates were collected at sites where historically large degradation compound concentrations were documented. Baked, pesticide-free sand (provided by the NWQL) was added to sample bottles containing NaHSO4 or pesticide-free water, and bottles containing only 5 mL pesticide-free water or NaHSO4 were included with sample sets for each sampling event. A sample of 1,3-DCP from a bulk distribution tank at Fort Hall was included in the October sampling. Water from the hot-water, high-pressure sprayer tank was included in the December sampling (water in the sprayer tank was not from the Fort Hall area).

Stainless steel scoops and stir bars were cleaned for reuse after each sampling event. Scoops, cleaned at the USGS Idaho District laboratory, were washed in a detergent solution, rinsed with deionized water, rinsed with methanol, rinsed with deionized water, air dried, and stored between sampling dates in ziplock bags. Stir bars were cleaned at the NWQL and returned to the Idaho District after each event.

RESULTS OF SOIL ANALYSES

One hundred and fourteen analyses were completed for this study (table 4, back of report), of which 104 were soil samples and 10 were samples of 1,3-DCP from bulk tank storage, commercially prepared pesticide-free water, commercially prepared NaHSO4, pesticide-free baked sand, and equipment rinsewater. Degradation products of 1,3-DCP or metam-sodium were detected in 42 of the 104 soil samples (detections are shown in red in table 4). Twenty-one of the 104 soil samples were prepared with NaHSO4 preservative (shown in blue in table 4). Twenty of the 104 soil samples were replicates, consisting of water-only or water versus NaHSO4 samples.

General Observations

Degradation products of 1,3-DCP and metam-sodium were detected in soil samples from September 1999. These results were somewhat unexpected because soil fumigants had not been applied to the area for at least 12 months prior to the September sampling. Although 1,2-dibromoethane (EDB) has not been used in the Fort Hall area for many years, it was unexpectedly detected in September, October, and March soil samples.

Effects of unusually dry weather conditions and an extended irrigation season during late summer and fall 1999 on pesticide detections are unknown. Percent moisture content in many March soil samples was greater than in September samples, and March samples generally effervesced less strongly when NaHSO4 was added than did September samples. Potential effects of greater soil moisture content on pesticide detections are unknown.

Diversity of 1,3-DCP degradation products was greatest and the concentrations were largest in soil samples from T8. The pesticide application history of this field has been documented by the Shoshone-Bannock Tribes since about 1995, but before this date, few records are available. No explanation currently is available for the diversity and concentrations of pesticide compounds detected in soil from this area.

Effects of Water Versus Sodium Bisulfate (NaHSO4) Preservative on Pesticide Detections

One or more of 9 pesticide degradation compounds were detected in samples from all trench areas and in 19 of 24 soil zones overall (table 4). One of the most important factors in detection of degradation compounds in soil was addition of NaHSO4 to the samples—compounds were detected in 95 percent of the samples (20 of 21) with NaHSO4 preservative added, either onsite or at the laboratory. Compounds were detected in only 27 percent of the samples (22 of 83) with water added.

Nine sets of paired water versus NaHSO4 replicate samples were collected. Degradation compounds were detected only in the NaHSO4-preserved samples in four of nine sets. Compounds were detected in both water and NaHSO4-preserved samples in four of nine

sets. In these latter four sets, concentrations generally were larger in samples with NaHSO4 than in samples with water, but concentrations in water-only replicate samples were similar. Compounds were detected in the water-only samples, but not in the NaHSO4 samples, in only one of the nine replicate sets (T6, 1-ft depth, September). NaHSO4 was not added to December 1999 samples, and degradation compounds were detected in samples from 2- and 3-ft depths at T7 and from all depths at T8.

The main objective of adding NaHSO4 to soil samples was to "reduce or eliminate the majority of the biological activity of the sample, thereby preventing biodegradation of the volatile target analytes" (U.S. Environmental Protection Agency, 1996, section 6.1.1.3). The effect of using water rather than NaHSO4 on biological activity (and potentially, on degradation or presence of pesticide compounds) of the samples is unknown. Original levels of biological activity in the soils are unknown, but biological activity in soil treated for years with fumigants may already be low or absent (J. Taberna, Sr., University of Idaho, Southwest Idaho Agricultural Research Center, Parma, Idaho, oral commun., 2000).

The greater number of compound detections in samples with NaHSO4 added may not be related to pH of the preservative or suppression of bacterial activity in the soil sample but may be caused by salts in the solution (sodium and sulfate) that strip pesticides from the soil particle surfaces (D. Rose, U.S. Geological Survey National Water Quality Laboratory, oral commun., October 2000).

The preceding observations are important because, even though pesticide-free water was added to most soil samples owing to strong reactions of soil carbonate minerals with the acidic preservative NaHSO4, compounds were most often detected in samples with NaHSO4 added. Nondetection of compounds in samples with water added does not necessarily indicate that the compounds were absent.

Because nondetection of degradation compounds in samples with water added is questionable and unreliable, no attempt was made to use the data for comparative trend analyses. Despite problems with comparability of analyses, the following generalizations can be made about the detected compounds.

Cis- and *trans*-dichloropropene (1,3-DCP)

Cis- and *trans*-1,3-DCP were the most commonly detected degradation compounds in soil samples and are the major components of commercial 1,3-DCP fumigant formulations. No EPA public drinking-water limits have been established for 1,3-DCP or its degradation products. These compounds have not been detected in ground water in the Fort Hall area.

- Most concentrations were less than the laboratory minimum reporting limit (mrl) of 0.07 and 0.13 µg/L for *cis*- and *trans*-isomers, respectively (concentrations below the mrl are indicated in table 4 by an 'e' preceding the value or by the word 'trace').
- 1,3-DCP compounds were detected in soil with either water or NaHSO4 added to samples, but compounds were most consistently detected when NaHSO4 was used.
- Concentrations of *cis*- and *trans*-DCP were largest in replicate samples with NaHSO4 added, collected from 2- and 3-ft depths at T8, March 2000.
- Detections of *cis*- and *trans*-DCP in the September laboratory replicate, water-only sample, from T6 (1-ft depth) are anomalous. Except for the September replicate sample, no degradation compounds were detected in soil from T6 during any other sampling event.

1,2,3-trichloropropane (1,2,3-TCP), 1,3-dichloropropane (1,3-DCP), 1,2,2-trichloropropane (1,2,2-TCP), and 1,1,2-trichloroethane (1,1,2-TCE)

These compounds were detected primarily in T8 samples and are suspected to be contaminants from earlier commercial formulations of 1,3-DCP (D. Rose, U.S. Geological Survey National Water Quality Laboratory, oral commun., October 2000). EPA public drinking-water limits have been established only for 1,1,2-trichloroethane (5 µg/L). These compounds have not been detected in ground water in the Fort Hall area.

- All compounds except 1,1,2-TCE were detected in T8 samples from all depths and most sampling events.

- Compounds were detected in T8 soil samples with either water or NaHSO4 solutions added.
- Concentrations of 1,2,3-TCP and 1,3-DCP generally were less than their mrls of 0.14 and 0.07 µg/L, respectively.
- 1,2,2-TCP and 1,1,2-TCE were detected primarily in samples from T8. Causes for detection of these compounds at T8 and not in other areas with histories of 1,3-DCP application are unknown.
- 1,2,2-TCP detected in T7 samples (3-ft depth in December and 2-ft depth in March) are anomalous. No other degradation products were detected in soil from T7.

Carbon Disulfide (CS2)

CS2 detected in most samples is suspected to be the result of, or to include, contamination from the NaHSO4 preservative rather than the degradation products of metam-sodium (D. Rose, U.S. Geological Survey National Water Quality Laboratory, oral commun., October 2000). No EPA public drinking-water limit has been established for CS2, and the compound has not been detected in ground water at Fort Hall.

- CS2 was detected in at least one soil sample from all trenches except T7.
- CS2 was detected in all samples with NaHSO4 added except for two—T1, 3-ft depth in October, and T6, 1 ft-depth in September.

Methyl Isothiocyanate (MITC)

MITC is a degradation product of metam-sodium. No EPA public drinking-water limit has been established for MITC, and the compound has not been detected in ground water at Fort Hall.

- MITC was detected in a few soil samples from T1 and T2, located in areas where historically, only 1,3-DCP has been applied. Causes for the consistent detection of MITC in soil samples from T1 and T2 are unknown.
- MITC was not detected in samples from T3 and T4, located in areas where historically, only metam-sodium has been applied.
- The largest concentration of MITC, 11 µg/L, was from T2 (1-ft sampling depth) in October 1999 (about 2 weeks after application of metam-sodium to nearby fields); all other concentrations were lower than the mrl of 1.8 µg/L.
- During March 2000 sampling, MITC was detected in soil from 1-ft depths at both T1 and T2 (NaHSO4 replicate samples), which indicates that this compound may persist in soil for extended periods of time.

1,2-Dibromoethane (EDB)

EDB historically has been a soil fumigant used in the Fort Hall area. An EPA public drinking-water limit of 0.05 µg/L has been established for EDB, and this compound has been detected in Fort Hall ground water in concentrations exceeding the EPA limit (Idaho District, USGS QWDATA data base).

- Detection of EDB in soil samples from T1 and T2 was unexpected because this compound has not been applied to croplands since the early 1990's.
- EDB was detected only in samples with NaHSO4 preservative added.
- Sources of the compound are unknown but may be caused by cropland irrigation with EDB-contaminated ground water.

SUMMARY AND SUGGESTIONS FOR FURTHER INVESTIGATIONS

The goal of the study was to determine potential risk of ground-water contamination from use of 1,3-DCP and metam-sodium on croplands near Fort Hall. Results of this study show that parent compounds or their degradation products can persist in soil 6 months or more after their application and are present to at least 3 ft below land surface in some areas.

- One hundred and four soil samples were analyzed for this study. Degradation products of 1,3-DCP or metam-sodium were detected in 42 of the 104 soil samples.
- In most cases, concentrations were at or near the laboratory minimum reporting limit for each compound. Detections of

pesticide degradation compounds in soil were not always consistent with reported histories of soil fumigant use or between croplands with similar soil characteristics.

- Compounds were detected more frequently in NaHSO4-preserved replicate samples—from all trench sites and sampling events—than in water-only replicate samples.
- Concentrations of these compounds were largest in soil samples from the T8 area, which has little historical documentation of pesticide use prior to 1995. Degradation products of 1,3-DCP or contaminants from earlier formulations of 1,3-DCP were present in soil to at least 3 ft below land surface at T8 and persisted through March 2000 sampling, at least 6 months after fall 1999 pesticide applications. It is unclear at this time whether the compounds detected in March were the result of the migration of pesticides applied in fall 1999 or whether the compounds have persisted from previous applications.
- MITC, a degradation product of metam-sodium, was detected in a few soil samples from T1 and T2, located in areas where historically, only 1,3-DCP has been applied. Causes for the persistence of MITC in soil samples from T1 and T2 areas are unknown.

Results of this study have produced a number of unanswered questions. The most significant questions relate to importance of compound detections from deep (3-ft) soil zones in some areas and mechanism(s) of compound transport. If compounds are consistently detected at 3-ft soil zones, are they migrating to underlying ground-water zones? If water is not an effective solvent for these compounds, how are they being transported through soil and unconsolidated sediments below the root zone? What other contaminants are present in soil and sediments and are potentially migrating to ground-water zones in the Fort Hall area? Additional studies of pesticide occurrence and persistence in soil and rock near Fort Hall may provide data to answer these questions.

One suggestion for further study is to analyze a column of soil (root zone) and sediments (rock underlying soil) for pesticides in an area where compounds have been consistently detected, such as at T8. The column would extend from land surface to the first water-bearing zone (35 to 50 ft below land surface), and samples would be collected for compound analyses at 1-ft intervals throughout the column. Additional tests could be developed to address questions about soil chemistry and soil/sediment characteristics related to possible downward movement of compounds in unsaturated materials. The study could be limited to selected analyses of a single column at a single site or could be expanded to include several columns in areas representing a variety of compounds, soil, sediment, and hydrogeologic conditions.

Additional studies could define migration of pesticides in soils representing broader types of cropland conditions and applications of pesticide compounds. Samples from many trenches could be analyzed during short periods of time, probably in late winter or early spring when soil moisture is high, before cropland irrigation has begun, and before crops are planted. Information on topics such as quality of irrigation water, water application practices, history of pesticide use, and farming practices for each site could be compiled, and these data could be compared with soil sample data for trend analyses.

Soil column or trench sampling could be coordinated with other soil research, such as the effect of pesticides on suppression of soil bacteria populations. The overall benefits of additional soil analyses studies would include acquisition of additional tools to help understand current pesticide migration problems, predict movement and effects of compounds, and manage ground-water resources in the area.

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Table 4. Laboratory analyses of soil samples from Fort Hall, Idaho, September 1999 through March 2000

Table 4. Laboratory analyses of soil samples from Fort Hall, Idaho, September 1999 through March 2000

[Analyses are reported in micrograms per liter (µg/L), equivalent to parts per billion; onsite, added at the time of sampling; lab, added at the U.S. Geological Survey National Water Quality Laboratory in Denver, Colorado; rep, replicate sample; numbers in red, detection of contaminant; NaHSO4, sodium bisulfate added to samples; <, less than; e or trace, less than laboratory minimum reporting limit; %, percent; n/a, not applicable; ---, compound not detected; g, grams; nanogram, 1 billionth of a gram]

Trench number and sample depths	Sample date	Solution added to sample	*cis* -1,3-dichloropropene (*cis* -1,3-DCP)	*trans* -1,3-dichloropropene (*trans* -1,3-DCP)	1,2,3-trichloropropane (1,2,3-TCP)	1,3-dichloropropane (1,3-DCP)	1,2,2-trichloropropane (1,2,2-TCP)	1,1,2-trichloroethane (1,1,2-TCE)	Carbon disulfide (CS2)	Methyl isothiocyanate (MITC)	1,2-dibromoethane (EDB)	Soil sample, weight (g)	Soil sample, % moisture
SOIL SAMPLES:													
T1- 1 foot	9/8/99	onsite NaHSO4	e0.18	0.23	<0.14	---	---	---	e0.22	< 1.8	e0.08	5.00	8.52
	10/19/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.40	8.59
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.30	8.17
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.30	7.48
onsite rep	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.50	7.48
onsite rep	3/23/00	onsite NaHSO4	0.30	0.30	<0.14	<0.07	---	---	e0.1242	e1.101	e0.0706	5.90	7.48
T1- 2 feet	9/8/99	onsite NaHSO4	e0.15	e0.21	<0.14	---	---	---	e0.14	< 1.8	e0.05	4.40	7.46
	10/19/99	onsite water	e0.12	e0.09	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.20	8.15
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.00	9.03
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	4.90	8.50
onsite rep	3/23/00	onsite NaHSO4	e0.1252	e0.1845	<0.14	<0.07	---	---	e0.0874	< 1.8	e0.0502	5.40	8.50
T1- 3 feet	9/8/99	onsite NaHSO4	e0.13	e0.13	<0.14	---	---	---	0.28	< 1.8	e0.04	4.80	1.63
	10/19/99	onsite water	e0.07	e0.06	<0.14	<0.07	---	---	e0.03	e0.20	<0.09	5.00	6.12
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.10	5.92
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.40	5.18
onsite rep	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.40	5.18
T2- 1 foot	9/8/99	onsite NaHSO4	0.29	0.32	<0.14	---	---	---	e0.19	< 1.8	e0.15	5.10	7.99
	10/19/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.40	8.19
lab rep	10/19/99	lab NaHSO4	e0.16	e0.19	<0.14	<0.07	---	---	0.31	11.00	e0.04	5.20	8.19
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.30	8.53
onsite rep	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.20	8.53
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.30	8.56
onsite rep	3/23/00	onsite NaHSO4	0.25	0.29	<0.14	<0.07	---	---	e0.0532	e0.4738	<0.09	5.10	8.56
T2- 2 feet	9/8/99	onsite NaHSO4	e0.12	e0.10	<0.14	---	---	---	e0.13	< 1.8	e0.08	5.70	6.80
	10/19/99	onsite water	e0.05	e0.05	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.20	6.89
onsite rep	10/19/99	onsite water	e0.06	e0.04	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.70	6.89
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.00	6.35
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.50	9.39
T2- 3 feet	9/8/99	lab water	<0.07	<0.13	<0.14	---	---	---	<0.08	< 1.8	<0.09	5.60	5.42
	10/19/99	onsite water	e0.14	e0.01	<0.14	<0.07	---	---	<0.08	e0.51	<0.09	5.10	8.94
lab rep	10/19/99	lab NaHSO4	e0.06	e0.07	<0.14	<0.07	---	---	e0.21	< 1.8	<0.09	5.10	8.94
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.20	5.64
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.50	5.48

Table 4. Laboratory analyses of soil samples from Fort Hall, Idaho, September 1999 through March 2000---Continued

Trench number and sample depths	Sample date	Solution added to sample	*cis* -1,3-dichloro-propene (*cis* -1,3-DCP)	*trans* -1,3-dichloro-propene (*trans* -1,3-DCP)	1,2,3-trichloro-propane (1,2,3-TCP)	1,3-dichloro-propane (1,3-DCP)	1,2,2-trichloro-propane (1,2,2-TCP)	1,1,2-trichloro-ethane (1,1,2-TCE)	Carbon disulfide (CS2)	Methyl isothio-cyanate (MITC)	1,2-dibromo-ethane (EDB)	Soil sample, weight (g)	Soil sample, % moisture
SOIL SAMPLES:													
T3- 1 foot	9/8/99	onsite NaHSO4	<0.07	e0.05	<0.14	---	---	---	e0.12	< 1.8	<0.09	5.10	7.32
	10/19/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.20	7.05
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.20	8.71
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.20	8.72
T3- 2 feet	9/8/99	onsite NaHSO4	<0.07	e0.07	<0.14	---	---	---	e0.15	< 1.8	<0.09	4.70	7.03
	10/19/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.20	9.00
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.20	7.49
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.10	6.41
T3- 3 feet	9/8/99	onsite NaHSO4	e0.06	e0.08	<0.14	---	---	---	0.33	< 1.8	<0.09	5.10	7.78
	10/19/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.00	7.29
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.60	6.85
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.30	5.69
T4- 1 foot	9/8/99	onsite NaHSO4	e0.09	e0.11	<0.14	---	---	---	e0.16	< 1.8	<0.09	5.60	7.40
	10/19/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	4.80	6.79
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.80	5.78
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.20	5.98
T4- 2 feet	9/8/99	onsite NaHSO4	<0.07	<0.13	<0.14	---	---	---	e0.14	< 1.8	<0.09	5.30	7.59
	10/19/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.10	4.36
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.70	5.98
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.70	5.16
T4- 3 feet	9/8/99	onsite NaHSO4	<0.07	<0.13	<0.14	---	---	---	0.29	< 1.8	<0.09	4.80	6.57
	10/19/99	onsite water	e0.03	trace	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.20	5.64
onsite rep	10/19/99	onsite water	trace	trace	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	4.90	5.64
lab rep	10/19/99	lab NaHSO4	e0.02	e0.04	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	4.90	5.64
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.20	6.01
onsite rep	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.40	6.01
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	4.90	6.04
T5- 1 foot	9/8/99	lab water	<0.07	<0.13	<0.14	---	---	---	<0.08	< 1.8	<0.09	5.50	9.63
T5- 2 feet	9/8/99	lab water	<0.07	<0.13	<0.14	---	---	---	<0.08	< 1.8	<0.09	5.00	9.96
T5- 3 feet	9/8/99	onsite NaHSO4	e0.04	e0.05	<0.14	---	---	---	e0.16	< 1.8	<0.09	5.60	4.85

Table 4. Laboratory analyses of soil samples from Fort Hall, Idaho, September 1999 through March 2000---Continued

Trench number and sample depths	Sample date	Solution added to sample	*cis* -1,3-dichloro-propene (*cis* -1,3-DCP)	*trans* -1,3-dichloro-propene (*trans* -1,3-DCP)	1,2,3-trichloro-propane (1,2,3-TCP)	1,3-dichloro-propane (1,3-DCP)	1,2,2-trichloro-propane (1,2,2-TCP)	1,1,2-trichloro-ethane (1,1,2-TCE)	Carbon disulfide (CS2)	Methyl isothio-cyanate (MITC)	1,2-dibromo-ethane (EDB)	Soil sample, weight (g)	Soil sample, % moisture
SOIL SAMPLES:													
T6- 1 foot	9/8/99	onsite NaHSO4	<0.07	<0.13	<0.14	---	---	---	<0.08	< 1.8	<0.09	5.30	13.10
lab rep	9/8/99	lab water	e0.14	e0.16	<0.14	---	---	---	0.68	< 1.8	<0.09	5.40	13.10
	10/19/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.40	8.25
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.50	7.92
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.00	17.61
T6- 2 feet	9/8/99	lab water	<0.07	<0.13	<0.14	---	---	---	<0.08	< 1.8	<0.09	5.30	13.56
	10/19/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.20	8.13
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.50	5.30
onsite rep	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.50	5.30
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.20	18.31
T6- 3 feet	9/8/99	lab water	<0.07	<0.13	<0.14	---	---	---	<0.08	< 1.8	<0.09	5.20	10.33
	10/19/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.30	4.45
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.20	3.70
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.10	10.54
T7- 1 foot	9/8/99	lab water	<0.07	<0.13	<0.14	---	---	---	<0.08	< 1.8	<0.09	5.30	17.39
	10/19/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	4.90	19.73
onsite rep	10/19/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	4.90	19.73
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.20	15.65
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.40	16.14
T7- 2 feet	9/8/99	lab water	<0.07	<0.13	<0.14	---	---	---	<0.08	< 1.8	<0.09	5.10	15.56
	10/19/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.10	18.30
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	4.80	17.43
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	e0.004	---	<0.08	< 1.8	<0.09	5.30	15.51
T7- 3 feet	9/8/99	lab water	<0.07	<0.13	<0.14	---	---	---	<0.08	< 1.8	<0.09	5.20	11.48
	10/19/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	4.60	15.10
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	e0.007	---	<0.08	< 1.8	<0.09	5.20	15.11
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.00	6.91

Table 4. Laboratory analyses of soil samples from Fort Hall, Idaho, September 1999 through March 2000---Continued

Trench number and sample depths	Sample date	Solution added to sample	*cis* -1,3-dichloro-propene (*cis* -1,3-DCP)	*trans* -1,3-dichloro-propene (*trans* -1,3-DCP)	1,2,3-trichloro-propane (1,2,3-TCP)	1,3-dichloro-propane (1,3-DCP)	1,2,2-trichloro-propane (1,2,2-TCP)	1,1,2-trichloro-ethane (1,1,2-TCE)	Carbon disulfide (CS2)	Methyl isothio-cyanate (MITC)	1,2-dibromo-ethane (EDB)	Soil sample, weight (g)	Soil sample, % moisture
SOIL SAMPLES:													
T8- 1 foot	10/19/99	onsite water	e0.09	e0.15	e0.20	e0.17	0.52	---	<0.08	< 1.8	<0.09	5.00	9.30
	12/7/99	onsite water	<0.07	<0.13	e0.05	e0.09	e0.01	---	<0.08	< 1.8	<0.09	5.40	8.75
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	e0.0125	---	<0.08	< 1.8	<0.09	5.80	11.08
onsite rep	3/23/00	onsite water	e0.0447	e0.0710	<0.14	<0.07	e0.0192	---	<0.08	< 1.8	<0.09	5.20	11.08
T8- 2 feet	10/19/99	onsite water	e0.06	e0.15	e0.07	e0.15	e0.13	---	<0.08	< 1.8	<0.09	4.90	8.15
	12/7/99	onsite water	<0.07	<0.13	<0.14	e0.06	e0.01	---	<0.08	< 1.8	<0.09	5.60	8.75
onsite rep	12/7/99	onsite water	<0.07	<0.13	<0.14	e0.09	e0.01	---	<0.08	< 1.8	<0.09	5.50	9.05
	3/23/00	onsite water	e0.0767	e0.1805	<0.14	e0.0658	e0.0185	---	<0.08	< 1.8	<0.09	4.90	11.04
onsite rep	3/23/00	onsite NaHSO4	2.54	3.52	e0.2333	e0.1559	e0.0361	---	0.52	< 1.8	<0.09	4.80	11.04
T8- 3 feet	10/19/00	onsite water	e0.07	0.27	e0.05	0.23	e0.21	---	<0.08	<1.8	<0.09	4.90	8.03
	12/7/99	onsite water	<0.07	<0.13	<0.14	0.23	e0.03	e0.03	e0.08	<1.8	<0.09	5.10	9.91
	3/23/00	onsite water	e0.0947	0.44	<0.14	e.0837	e0.0182	---	<0.08	< 1.8	<0.09	5.50	11.23
onsite rep	3/23/00	onsite water	e0.1070	0.37	<0.14	e0.0970	e0.0218	---	<0.08	< 1.8	<0.09	5.30	11.23
onsite rep	3/23/00	onsite NaHSO4	2.06	2.79	<0.14	e0.1390	e0.0332	---	0.65	< 1.8	<0.09	5.50	11.23
OTHER SAMPLES:													
1,3-dichloro-propene (bulk)	10/19/99	1,3-DCP only	5.37 (nanograms)	5.09 (nanograms)	---	---	---	---	---	---	---	---	---
pesticide-free water	10/19/99	water only	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	n/a	n/a
	12/7/99	water only	<0.07	<0.13	<0.14	<0.07	---	---	e0.04	< 1.8	<0.09	n/a	n/a
	3/23/00	water only	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	n/a	n/a
sodium bisulfate	9/8/99	NaHSO4 only	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	n/a	n/a
pesticide-free baked sand	9/8/99	onsite NaHSO4	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.00	1.58
	10/22/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.10	1.58
	12/7/99	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.50	1.58
	3/23/00	onsite water	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	5.30	1.58
equipment rinse-water	12/7/99	rinsewater only	<0.07	<0.13	<0.14	<0.07	---	---	<0.08	< 1.8	<0.09	n/a	n/a

Appendix A. Excerpts from U.S. Environmental Protection Agency Method 5035

http://www.epa.gov/epaoswer/hazwaste/test/5035.pdf

Abbreviations and Conversions:

°C, degrees Celsius [°F=(1.8)(°C)+32]
cm, centimeter (multiply by 0.3937 to obtain inch)
µg/kg, microgram per kilogram

METHOD 5035

CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Refer to the introductory material in this chapter, Organic Analytes, Sec. 4.1, for general sample collection information. The low concentration portion of this method employs sample vials that are filled and weighed in the field and never opened during the analytical process. As a result, sampling personnel should be equipped with a portable balance capable of weighing to 0.01 g.

6.1 Preparation of sample vials

The specific preparation procedures for sample vials depend on the expected concentration range of the sample, with separate preparation procedures for low concentration soil samples and high concentration soil and solid waste samples. Sample vials should be prepared in a fixed laboratory or other controlled environment, sealed, and shipped to the field location. Gloves should be worn during the preparation steps.

6.1.1 Low concentration soil samples

The following steps apply to the preparation of vials used in the collection of low concentration soil samples to be analyzed by the closed-system purge-and-trap equipment described in Method 5035.

6.1.1.1 Add a clean magnetic stirring bar to each clean vial. If the purge-and-trap device (Sec. 4.2) employs a means of stirring the sample other than a magnetic stirrer (e.g., sonication or other mechanical means), then the stir bar is omitted.

6.1.1.2 Add preservative to each vial. The preservative is added to each vial prior to shipping the vial to the field. Add approximately 1 g of sodium bisulfate to each vial. If samples markedly smaller or larger than 5 g are to be collected, adjust the amount of preservative added to correspond to approximately 0.2 g of preservative for each 1 g of sample. Enough sodium bisulfate should be present to ensure a sample pH of ≤2.

6.1.1.3 Add 5 mL of organic-free reagent water to each vial. The water and the preservative will form an acid solution that will reduce or eliminate the majority of the biological activity in the sample, thereby preventing biodegradation of the volatile target analytes.

6.1.1.4 Seal the vial with the screw-cap and septum seal. If the double-ended, fritted, vials are used, seal both ends as recommended by the manufacturer.

6.1.1.5 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.1.6 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

6.1.1.7 Because volatile organics will partition into the headspace of the vial from the aqueous solution and will be lost when the vial is opened, surrogates, matrix spikes, and internal standards (if applicable) should only be added to the vials after the sample has been added to the vial. These standards should be introduced back in the laboratory, either manually by

puncturing the septum with a small-gauge needle or automatically by the sample introduction system, just prior to analysis.

6.1.2 High concentration soil samples collected without a preservative

When high concentration samples are collected without a preservative, a variety of sample containers may be employed, including 60-mL glass vials with septum seals (see Sec. 4.4).

6.1.3 High concentration soil samples collected and preserved in the field

The following steps apply to the preparation of vials used in the collection of high concentration soil samples to be preserved in the field with methanol and analyzed by the aqueous purge-and-trap equipment described in Method 5030.

6.1.3.1 Add 10 mL of methanol to each vial.

6.1.3.2 Seal the vial with the screw-cap and septum seal.

6.1.3.3 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.3.4 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

NOTE: Vials containing methanol should be weighed a second time on the day that they are to be used. Vials found to have lost methanol (reduction in weight of >0.01 g) should not be used for sample collection.

6.1.3.5 Surrogates, internal standards and matrix spikes (if applicable) should be added to the sample after it is returned to the laboratory and prior to analysis.

6.1.4 Oily waste samples

When oily waste samples are known to be soluble in methanol or PEG, sample vials may be prepared as described in Sec. 6.1.3, using the appropriate solvent. However, when the solubility of the waste is unknown, the sample should be collected without the use of a preservative, in a vial such as that described in Sec. 6.1.2.

6.2 Sample collection

Collect the sample according to the procedures outlined in the sampling plan. As with any sampling procedure for volatiles, care must be taken to minimize the disturbance of the sample in order to minimize the loss of the volatile components. Several techniques may be used to transfer a sample to the relatively narrow opening of the low concentration soil vial.

These include devices such as the EnCore™ sampler, the Purge-and-Trap Soil Sampler™, and a cut plastic syringe. Always wear gloves whenever handling the tared sample vials.

6.2.1 Low concentration soil samples

6.2.1.1 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed

to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

6.2.1.2 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the sample vial containing the preservative solution. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4°C.

NOTE: Soil samples that contain carbonate minerals (either from natural sources or applied as an amendment) may effervesce upon contact with the acidic preservative solution in the low concentration sample vial. If the amount of gas generated is very small (i.e., several mL), any loss of volatiles as a result of such effervescence may be minimal if the vial is sealed quickly. However, if larger amounts of gas are generated, not only may the sample lose a significant amount of analyte, but the gas pressure may shatter the vial if the sample vial is sealed. Therefore, when samples are known or suspected to contain high levels of carbonates, a test sample should be collected, added to a vial, and checked for effervescence. If a rapid or vigorous reaction occurs, discard the sample and collect low concentration samples in vials that do not contain the preservative solution.

6.2.1.3 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

6.2.1.4 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

6.2.1.5 As with the collection of aqueous samples for volatiles, collect at least two replicate samples. This will allow the laboratory an additional sample for reanalysis. The second sample should be taken from the same soil stratum or the same section of the solid waste being sampled, and within close proximity to the location from which the original sample was collected.

6.2.1.6 In addition, since the soil vial cannot be opened without compromising the integrity of the sample, at least one additional aliquot of sample must be collected for screening, dry weight determination, and high concentration analysis (if necessary). This third aliquot may be collected in a 60-mL glass vial or a third 40-mL soil sample vial. However, this third vial must *not* contain the sample preservative solution, as an aliquot will be used to determine dry weight. If high concentration samples are collected in vials containing methanol, then two additional aliquots should be collected, one for high concentration analysis collected in a vial containing methanol, and another for the dry weight determination in a vial without either methanol or the low concentration aqueous preservative solution.

6.2.1.7 If samples are known or expected to contain target analytes over a wide range of concentrations, thereby requiring the analyses of multiple sample aliquots, it may be advisable and practical to take an additional sample aliquot in a low concentration soil vial containing the preservative, but collecting only 1-2 g instead of the 5 g collected in Sec. 6.2.1.1. This aliquot may be used for those analytes that exceed the instrument calibration range in the 5-g analysis.

6.2.1.8 The EnCore™ sampler has not been thoroughly evaluated by EPA as a sample storage device. While preliminary results indicate that storage in the EnCore™ device may

be appropriate for up to 48 hours, samples collected in this device should be transferred to the soil sample vials as soon as possible, or analyzed within 48 hours.

6.2.1.9 The collection of low concentration soil samples in vials that contain methanol is not appropriate for samples analyzed with the closed-system purge-and-trap equipment described in this method (see Sec. 6.2.2).

6.2.2 High concentration soil samples preserved in the field

The collection of soil samples in vials that contain methanol has been suggested by some as a combined preservation and extraction procedure. However, this procedure is not appropriate for use with the low concentration soil procedure described in this method.

NOTE: The use of methanol preservation has not been formally evaluated by EPA and analysts must be aware of two potential problems. First, the use of methanol as a preservative and extraction solvent introduces a significant dilution factor that will raise the method quantitation limit beyond the operating range of the low concentration direct purge-and-trap procedure (0.5-200 µg/kg). The exact dilution factor will depend on the masses of solvent and sample, but generally exceeds 1000, and may make it difficult to demonstrate compliance with regulatory limits or action levels for some analytes. Because the analytes of interest are volatile, the methanol extract cannot be concentrated to overcome the dilution problem. Thus, for samples of unknown composition, it may still be necessary to collect an aliquot for analysis by this closed-system procedure and another aliquot preserved in methanol and analyzed by other procedures. The second problem is that the addition of methanol to the sample is likely to cause the sample to fail the ignitability characteristic, thereby making the unused sample volume a hazardous waste.

6.2.2.1 When samples are known to contain volatiles at concentrations high enough that the dilution factor will not preclude obtaining results within the calibration range of the appropriate determinative method, a sample may be collected and immediately placed in a sample vial containing purge-and-trap grade methanol.

6.2.2.2 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

6.2.2.3 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the vial containing 10 mL of methanol. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4°C.

6.2.2.4 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

6.2.2.5 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

6.2.2.6 Other sample weights and volumes of methanol may be employed, provided that the analyst can demonstrate that the sensitivity of the overall analytical procedure is appropriate for the intended application.

6.2.2.7 The collection of at least one additional sample aliquot is required for the determination of the dry weight, as described in Sec. 6.2.1.6. Samples collected in methanol should be shipped as described in Sec. 6.3, and must be clearly labeled as containing methanol, so that the samples are not analyzed using the closed-system purge-and-trap equipment described in this procedure.

6.2.3 High concentration soil samples not preserved in the field

The collection of high concentration soil samples that are not preserved in the field generally follows similar procedures as for the other types of samples described in Secs. 6.2.1 and 6.2.2, with the obvious exception that the sample vials contain neither the aqueous preservative solution nor methanol. However, when field preservation is not employed, it is better to collect a larger volume sample, filling the sample container as full as practical in order to minimize the headspace. Such collection procedures generally do not require the collection of a separate aliquot for dry weight determination, but it may be advisable to collect a second sample aliquot for screening purposes, in order to minimize the loss of volatiles in either aliquot.

6.2.4 Oily waste samples

The collection procedures for oily samples depend on knowledge of the waste and its solubility in methanol or other solvents.

6.2.4.1 When an oily waste is known to be soluble in methanol or PEG, the sample may be collected in a vial containing such a solvent (see Sec. 6.1.4), using procedures similar to those described in Sec. 6.2.2.

6.2.4.2 When the solubility of the oily waste is not known, the sample should either be collected in a vial without a preservative, as described in Sec. 6.2.3, or the solubility of a trial sample should be tested in the field, using a vial containing solvent. If the trial sample is soluble in the solvent, then collect the oily waste sample as described in Sec. 6.2.2. Otherwise, collect an unpreserved sample as described in Sec. 6.2.3.

6.3 Sample handling and shipment

All samples for volatiles analysis should be cooled to approximately 4°C, packed in appropriate containers, and shipped to the laboratory on ice, as described in the sampling plan.

6.4 Sample storage

6.4.1 Once in the laboratory, store samples at 4°C until analysis. The sample storage area should be free of organic solvent vapors.

6.4.2 All samples should be analyzed as soon as practical, and within the designated holding time from collection. Samples not analyzed within the designated holding time must be noted and the data are considered minimum values.

6.4.3 When the low concentration samples are strongly alkaline or highly calcareous in nature, the sodium bisulfate preservative solution may not be strong enough to reduce the pH of the soil/water solution to below 2. Therefore, when low concentration soils to be sampled are known or suspected to be strongly alkaline or highly calcareous, additional steps may be required to preserve the samples. Such steps include: addition of larger amounts of the sodium bisulfate preservative to non-calcareous samples, storage of low concentration samples at -10°C (taking care not to fill the vials so full that the expansion of the water in the vial breaks the vial), or significantly reducing the

maximum holding time for low concentration soil samples. Whichever steps are employed, they should be clearly described in the sampling and QA project plans and distributed to both the field and laboratory personnel. See Sec. 6.2.1.2 for additional information.

Appendix B. U.S. Geological Survey Laboratory Memorandum, Description of Custom Method

Abbreviations and Conversions:

°C, degrees Celsius [°F=(1.8)(°C)+32]
centimeter (multiply by 0.3937 to obtain inch)
meter (multiply by 3.281 to obtain foot)
mm (millimeter, multiply by 0.03937 to obtain inch)
µm, micrometer
ug/kg, microgram per kilogram

Memorandum

Date: 11/29/99

To: Deb Parliman

Cc: Ralph White

From: Donna Rose

RE: Proposal CL99II- Analysis of MITC and other VOCs in soils from Idaho by purge and trap GC/MS

DESCRIPTION OF CUSTOM METHOD FOR LAB CODE 8133:

Soil samples received from the Idaho district were analyzed according to U. S. Environmental Protection Agency (USEPA) Method 5035 (December 1996, Revision 0). Five grams of soil were added in the field to a vial containing five milliliters (mLs) of water, 1 gram of sodium bisulfate as a preservative, and a magnetic stir bar. The sodium bisulfate preservative was omitted for those samples that contained high amounts of carbonate minerals per method 5035 (Section 6.2.1.2). The vial was sealed, and sent to the laboratory in a cooler. Samples were stored at 4°C until analysis. Percent moisture was determined using an infra-red balance. Instrument operating conditions are listed in Table 1. Compound identifications and quantitations were determined according to Connor and others, 1998. The quantitation ions, qualification ions, and calibration ranges are listed in Table 2.

Table 1: Instrument Operating Conditions for LC 8133

Autosampler	**Varian Archon Autosampler**, chilled to 4°C, Soil mode operation
Sample Preheat Temp	40 ˚C
Preheat Time	3 minutes
Purge & Trap Concentrator	**Tekmar Liquid Sample Concentrator, Model 3000**
Trap	Supelco Vocarb 3000
Purge	11 minutes
Dry Purge	3 minutes
Desorb Preheat	245 ˚C
Desorb	3 minutes at 250 ˚C
Bake	17 minutes at 260 ˚C
Gas Chromatograph	**Hewlett Packard 5890 Gas Chromatograph**, split/splitless mode
Column	60 meter, 0.25 mm inner diameter, 1.4 µm film thickness, RTX 624
Initial Temperature	35 ˚C for 8 minutes
Temperature ramp	8.0 ˚C/minute to 200˚C
Final temperature/time	200˚C for 12 minutes
Mass Spectrometer	**Hewlett Packard 5971 Mass selective detector**, electron impact mode
Scan range	41 atomic mass units (amu) to 310 amu

Table 2: Quantitation Ions, Identification Ions, and Calibration Ranges for LC 8133

{n/a, not applicable}

Compound	Quantitation Ion (mass/charge)	Qualifying Ions (mass/charge)	Calibration Range (nanograms)
Carbon disulfide	76	78	1 to 200
cis 1,3-Dichloropropene	110	75,49	1 to 200
trans 1,3-Dichloropropene	110	75,49	1 to 200
1,3-Dichloropropane	76	78,63	1 to 200
1,2-Dibromoethane	107	109	1 to 200
1,2,3-Trichloropropane	110	112,99	1 to 200
Methyl isothiocyanate (MITC)	73	72,45	3.1 to 620
1,2-Dichloroethane d4, surrogate	65	67, 102	n/a
Toluene d8, surrogate	98	100, 70	n/a
1,4-Bromofluorobenzene, surrogate	95	174,176	n/a
Fluorobenzene, internal standard	96	70, 50	n/a

Short-Term Method Detection Level, and Laboratory Report Level (LRL)

The short-term method detection levels (MDL's) were calculated for each compound according to the procedure in CFR § 136 Appendix B. The MDL samples were prepared by adding 5.0 grams of Ottawa sand, previously burned, to a vendor prepared (Eagle Picher) soil VOC vial containing 5.0 mLs of water, 1.0 gram of sodium bisulfate preservative, and a magnetic stir bar. One microliter of the calibration standard was spiked into the water, with the needle of the syringe placed about two centimeters below the surface of the water. The vial was capped, and placed in the autosampler for analysis. A total of nine MDL samples were prepared and analyzed on three separate days (3 samples per day).

The laboratory report level (LRL) for all compounds is calculated as two times the short-term MDL for this custom lab code. As the method progresses, and long-term data are available, the LRL may be re-evaluated using the long-term MDL. Refer to U. S. Geological Survey Open-File Report 99-193 for information on determining long-term MDLs, and LRLs (Childress, et al, 1999). Refer to Table 3 for short-term MDLs, and LRLs for LC 8133.

Table 3: Short-Term Method Detection Levels, and Laboratory Report Levels

Compound	MDL for 9 Replicates ug/kg	Laboratory Report Level (LRL) ug/kg	Standard Deviation ug/kg	Amount Spiked ug/kg
Carbon disulfide	0.04	<0.08	0.0129	0.2
cis 1,3-Dichloropropene	0.04	<0.07	0.0123	0.2
trans 1,3-Dichloropropene	0.07	<0.13	0.0228	0.2
1,3-Dichloropropane	0.04	<0.07	0.0122	0.2
1,2-Dibromoethane	0.04	<0.09	0.0151	0.2
1,2,3-Trichloropropane	0.07	<0.14	0.0248	0.2
Methyl isothiocyanate (MITC)	0.9	<1.8	0.3126	0.62

Quality Control:

Several types of quality control samples are analyzed along with the samples to ensure high quality data. Quality control samples consist of continuing calibration verification standards (CCVs), set blanks, set spikes, matrix spikes, and laboratory reporting level (LRL) check standards.

Continuing Calibration Verification Standards (CCVs) - reported in percent recovery
CCVs are analyzed throughout the run, or at least every 12th injection.

Set blanks- reported in ug/Kg
Sample results are not blank-subtracted. Sample results, that are not significantly different from the bracketing set blanks, will be censored. Set blanks are analyzed throughout the run, or at least after every CCV.

Set Spike- reported in percent recovery
The set spike is prepared from a different source than the calibration standards. Sample results are not corrected for poor set spike recoveries.

Matrix Spike- reported in percent recovery.
Samples chosen at random were spiked at the same level as the CCVs, and analyzed. Sample results are not corrected for poor matrix spike recoveries. A poor recovery will provide information on how the particular compound reacts in the particular matrix.

Laboratory Reporting Level (LRL) check standard- reported percent recovery
LRLs are spiked at the level of the lowest calibration standard, and analyzed at the beginning of the run, and the end of the run, to verify the compound can be detected at this low level, and to verify the quantitation at this low level.

Bias and Variability Data:

Several types of bias and variability data are reported in Tables 4, 5, 6, 7, 8, and 9. Data for Ottawa sand spiked at two levels, and analyzed over several days is reported in Tables 4 and 5. Bias and variability data is also reported for the CCVs in Table 6. Data

for the LRLs is reported in Table 7. Data for the set spikes are reported in Table 8. Data for soils chosen at random, and spiked at the laboratory are reported in Table 9.

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Table 4: Bias and Variability for Replicate Spikes in Ottawa Sand Spiked from 2.0 to 6.2 ug/kg

Analyzed from September 9, 1999 through October 25, 1999

Compound	Amount Spiked ug/kg	Average Percent Recovery	Std Dev Percent	Rel Std Deviation Percent	Number of spikes
Carbon disulfide	2.0	105	6	5	11
cis 1,3-Dichloropropene	2.0	106	7	6	11
trans 1,3-Dichloropropene	2.0	104	6	5	11
1,3-Dichloropropane	2.0	108	4	4	11
1,2-Dibromoethane	2.0	110	5	4	11
1,2,3-Trichloropropane	2.0	108	6	5	11
Methyl isothiocyanate (MITC)	6.2	117	11	10	11

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Table 5: Bias and Variability for Low Level Ottawa Sand Spikes
Spiked from 0.2 to 0.62 ug/kg

Analyzed from September 9, 1999 through October 25, 1999

Compound	Amount Spiked ug/kg	Average Percent Recovery	Std Dev Percent	Rel Std Deviation Percent	Number of spikes
Carbon disulfide	0.2	109	13	12	11
cis 1,3-Dichloropropene	0.2	119	11	9	11
trans 1,3-Dichloropropene	0.2	115	13	11	11
1,3-Dichloropropane	0.2	117	6	5	11
1,2-Dibromoethane	0.2	113	8	7	11
1,2,3-Trichloropropane	0.2	123	14	12	11
Methyl isothiocyanate (MITC)	0.62	159[1]	53	34	11

[1] An interfering column bleed peak elutes slightly to the right of MITC, resulting in higher recoveries and standard deviation at this low level.

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Table 6: Bias and Variability for Continuing Calibration Verification Standards
Spiked from 2.0 to 6.2 ug/kg

Analyzed from September 9, 1999 through October 25, 1999

Compound	Amount Spiked ug/kg	Average Percent Recovery	Std Dev Percent	Rel Std Deviation Percent	Number of CCVs
Carbon disulfide	2.0	94	5	5	19
cis 1,3-Dichloropropene	2.0	95	8	8	19
trans 1,3-Dichloropropene	2.0	93	6	7	19
1,3-Dichloropropane	2.0	96	7	7	19
1,2-Dibromoethane	2.0	97	8	8	19
1,2,3-Trichloropropane	2.0	95	8	9	19
Methyl isothiocyanate (MITC)	6.2	95	9	10	19

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Table 7: Bias and Variability for Laboratory Report Level Check Standards
Spiked from 0.2 to 0.62 ug/kg

Analyzed from September 9, 1999 through October 25, 1999

Compound	Amount Spiked ug/kg	Average Percent Recovery	Std Dev Percent	Rel Std Deviation Percent	Number of LRLs
Carbon disulfide	0.2	95	11	11	5
cis 1,3-Dichloropropene	0.2	103	8	8	5
trans 1,3-Dichloropropene	0.2	95	11	12	5
1,3-Dichloropropane	0.2	99	10	10	5
1,2-Dibromoethane	0.2	96	10	10	5
1,2,3-Trichloropropane	0.2	105	10	9	5
Methyl isothiocyanate (MITC)	0.62	129	24	19	5

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Table 8: Bias and Variability for Set Spikes
Spiked from 1.0 to 4.0 ug/kg

Analyzed from September 9, 1999 through October 25, 1999

Compound	Amount Spiked ug/kg	Average Percent Recovery	Std Dev Percent	Rel Std Deviation Percent	Number of set spikes
Carbon disulfide	1.6	97	15	15	7
cis 1,3-Dichloropropene	1.8	92	8	8	7
trans 1,3-Dichloropropene	2.6	83	8	9	7
1,3-Dichloropropane	2.4	94	7	8	7
1,2-Dibromoethane	1.0	90	7	8	7
1,2,3-Trichloropropane	4.0	78	9	12	7
Methyl isothiocyanate (MITC)	not spiked	n/a	n/a	n/a	0

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Table 9: Bias and Variability for Soils from Ft. Hall Project

Soil Samples Chosen at Random, Spiked in the laboratory at 2.0 to 6.2 ug/kg

Analyzed from September 14, 1999 through October 21, 1999

Compound	Amount Spiked ug/kg	Average Percent Recovery	Std Dev Percent	Rel Std Deviation Percent	Count
Carbon disulfide	2.0	90	11	12	4
cis 1,3-Dichloropropene	2.0	74	19	25	4
trans 1,3-Dichloropropene	2.0	75	15	20	4
1,3-Dichloropropane	2.0	82	12	15	4
1,2-Dibromoethane	2.0	79	11	14	4
1,2,3-Trichloropropane	2.0	75	14	18	4
Methyl isothiocyanate[1] (MITC)	6.2	58	41	70	4

[1]One of the four samples had only 3% recovery, with the other samples recovering at 101%, 63%, and 63%.

Analyst's Notes

A small amount of mass 73, due to an interfering column bleed peak, was present in the retention time window for MITC. The amount was quantitated, and treated as a "blank" contaminant.

Carbon disulfide was also detected in small amounts in some of the set blanks. The presence of carbon disulfide may be a byproduct from the sodium bisulfate preservative. Blanks without the preservative were analyzed, and did not contain carbon disulfide.

REPORTS:

Individual reports for each sample are being provided electronically in an Excel workbook, via email.

REFERENCES:

Childress, C. J., Foreman, W. T., Connor, B. F., and Maloney, T. J., 1999, "New Reporting Procedures Based on Long-Term Method Detection Levels and Some Considerations for Interpretations of Water-Quality Data Provided by the U. S. Geological Survey National Water Quality Laboratory", 19 pages.

Connor, B.F., Rose, Donna L., Noriega, Mary C., Murtagh, Lucinda K., and Abney, Sonja R., 1998, "Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of 86 Volatile Organic Compounds in Water by Gas Chromatography/Mass Spectrometry, Including Detections Less Than Reporting Limits", 78 pages.

U. S. Environmental Protection Agency, 1992, Guidelines establishing test procedures for the analysis of pollutants (Part 136, Appendix B. Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11): U. S. code of Federal Regulations, Title 40, revised as of July 1, 1992, p. 565-567.

U. S. Environmental Protection Agency, 1996, Method 5035—Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples: CD-ROM Revision 0, December 1996, 24 pages.