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# **EVALUATION OF ARCHIVED WATER SAMPLES USING CHLORINE ISOTOPIC DATA, IDAHO NATIONAL ENGINEERING AND ENVIRONMENTAL LABORATORY, IDAHO, 1966-93**

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 98-4008

Prepared in cooperation with the  
U.S. DEPARTMENT OF ENERGY



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LABORATORY, IDAHO, 1966-93**

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**Idaho Falls, Idaho  
1998**

U.S. DEPARTMENT OF THE INTERIOR  
BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY  
Thomas J. Casadevall, Acting Director

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## CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATED UNITS

<u>Multiply</u>	<u>By</u>	<u>To obtain</u>
meter (m)	3.281	foot
kilometer (km)	0.622	mile
square kilometer (km <sup>2</sup> )	0.386	square mile
liter (L)	0.264	gallon
kilogram	2.204	pound
becquerel/liter	27.03	picocuries/liter

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 both the United States and Canada.

Abbreviated units used in report: mg/L (milligram per liter), g (gram), atoms/L (atoms per liter),  $\delta$  (delta),  $\mu\text{S/cm}$  (microsiemens per centimeter at 25 °C), Bq/L (Becquerel/liter), p (proton), n (neutron),  $\alpha$  (alpha particle),  $\gamma$  (gamma radiation),  $\mu$  (muon), Mohm (mega ohms), min (minute), sec (second), mL (milliliter), ° (degrees).

# Evaluation of Archived Water Samples Using Chlorine Isotopic Data, Idaho National Engineering and Environmental Laboratory, Idaho, 1966–93

## Abstract

Since 1966, the U.S. Geological Survey (USGS) routinely has archived at least one suite of quarterly ground- and surface-water samples collected at the Idaho National Engineering and Environmental Laboratory (INEEL) each year. The samples and a large associated database are available for research purposes. To evaluate the suitability of the samples as an indicator of historical radionuclide concentrations, archived-water samples collected from six USGS monitoring wells from 1966–93 and one surface-water site for 1970 were analyzed for stable chlorine isotopic ratios, chlorine-37/chlorine-35 ( $^{37}\text{Cl}/^{35}\text{Cl}$ ). These ratios may be useful in determining if fractionation of chlorine isotopes has occurred during storage or if mixing has occurred along a flowpath in the eastern Snake River Plain aquifer at the INEEL. This information is useful in evaluating if radioactive chlorine ( $^{36}\text{Cl}$ ) concentrations measured in water from the archive samples in the 1990's are representative of the historical concentration at the time of sample collection.

The  $^{37}\text{Cl}/^{35}\text{Cl}$  ratio of the archived samples was measured at the Environmental Isotope Laboratory at the University of Waterloo, Ontario, Canada, and was compared to the  $^{37}\text{Cl}/^{35}\text{Cl}$  of Standard Mean Ocean Chloride. The resultant delta  $^{37}\text{Cl}$  ( $\delta^{37}\text{Cl}$ ) ranged from -0.44 to +0.59 permil. The largest variation in  $\delta^{37}\text{Cl}$  for water from any individual well was 0.91 permil. The small range of positive  $\delta^{37}\text{Cl}$  values are indicative of an environmental setting having little or no measurable fractionation of stable chlorine isotopes. Negative  $\delta^{37}\text{Cl}$  values were attributed to wastewater disposed at the INEEL and not to any processes operational during sample storage in the archive library or along the flowpath in the Snake River Plain aquifer.

Chlorine-36 concentrations also were measured in the archive ground-water samples selected for this evaluation. The historical  $^{36}\text{Cl}$  concentrations ranged from  $1.1 \pm 0.1 \times 10^8$  atoms/liter to

$28,000 \pm 910 \times 10^8$  atoms/liter. Based on the evaluation of the archived-water samples in terms of  $\delta^{37}\text{Cl}$ , it was concluded that the  $^{36}\text{Cl}$  concentrations measured in 1993 were representative of the concentrations at the time of sample collection.

## INTRODUCTION

The Idaho National Engineering and Environmental Laboratory (INEEL) is located in southeastern Idaho and is one of the largest of the United States Department of Energy's (DOE) nuclear testing facilities, covering about 2,300 km<sup>2</sup> (fig. 1). The INEEL was commissioned in 1949 for the construction and testing of nuclear reactors. Since 1952, there have been 52 different reactors constructed and tested at this site and 13 of the reactors were still operable in 1996 (John Walsh, Lockheed-Martin, written commun., 1996).

The DOE requires information about the mobility and/or retardation of radiochemical and chemical wastes released to the environment at the INEEL. In 1949, the DOE (then called the Atomic Energy Commission) requested the U. S. Geological Survey (USGS) to describe the geology and water resources of the eastern Snake River Plain. Since the completion of that initial site characterization, the USGS has maintained a network of monitoring wells to determine hydrologic trends and to describe the fate of contaminants contained in wastewater released to the environment.

Between 1953 and February 1984, low-level radioactive wastewater containing tritium ( $^3\text{H}$ ), chlorine-36 ( $^{36}\text{Cl}$ ), and iodine-129 ( $^{129}\text{I}$ ), among other radiochemical and chemical constituents, was routinely discharged to the eastern Snake River Plain aquifer through a 183-m-deep disposal well at the Idaho Chemical Processing Plant (ICPP) (fig. 2). Additionally, wastewater has been discharged to the environment through disposal ponds at the Test Reactor Area (TRA) (fig. 2) since 1952 and at the ICPP since February 1984 (Cecil and others, 1992).

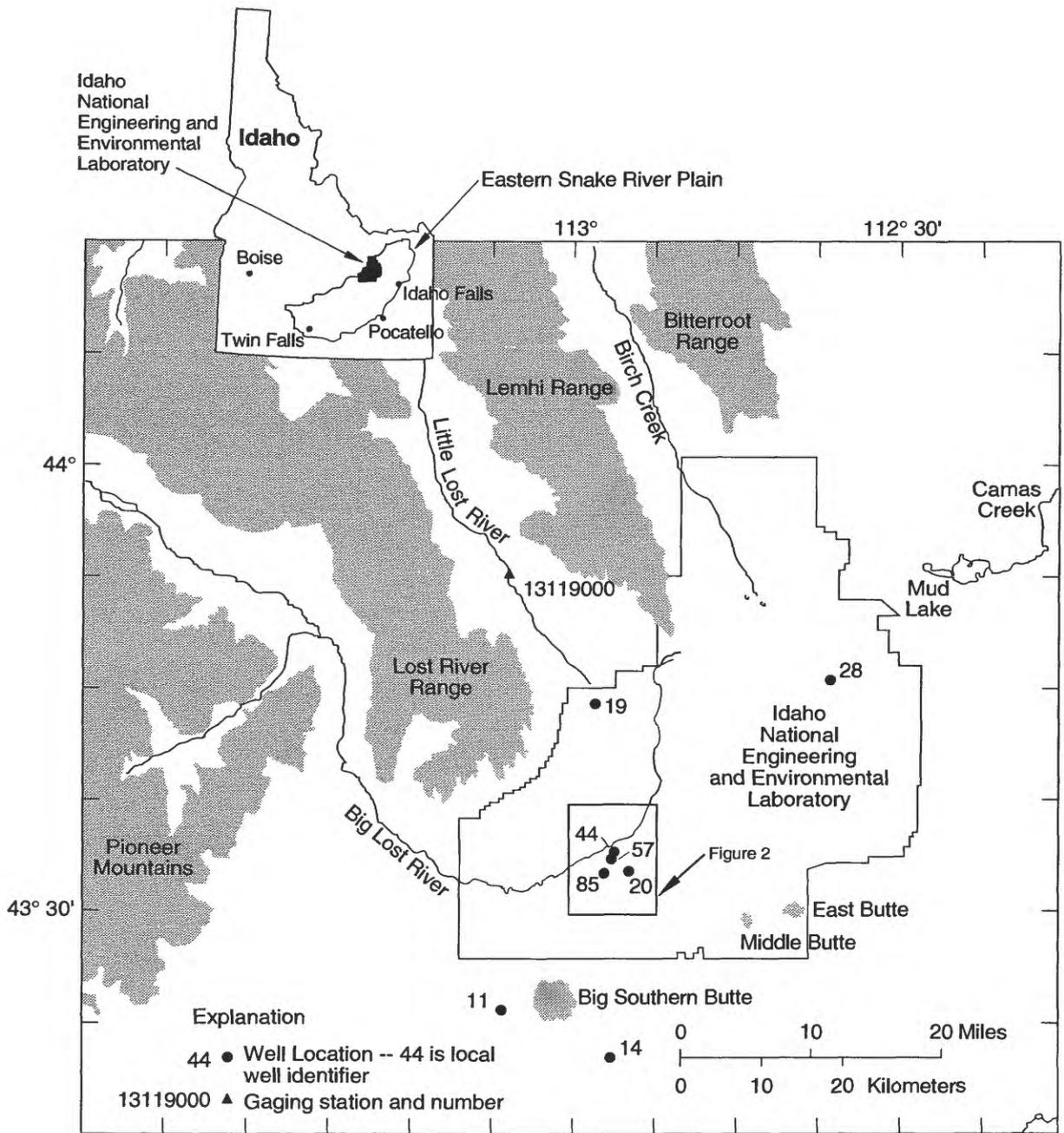


Figure 1. Location of the Idaho National Engineering and Environmental Laboratory and selected observation wells.

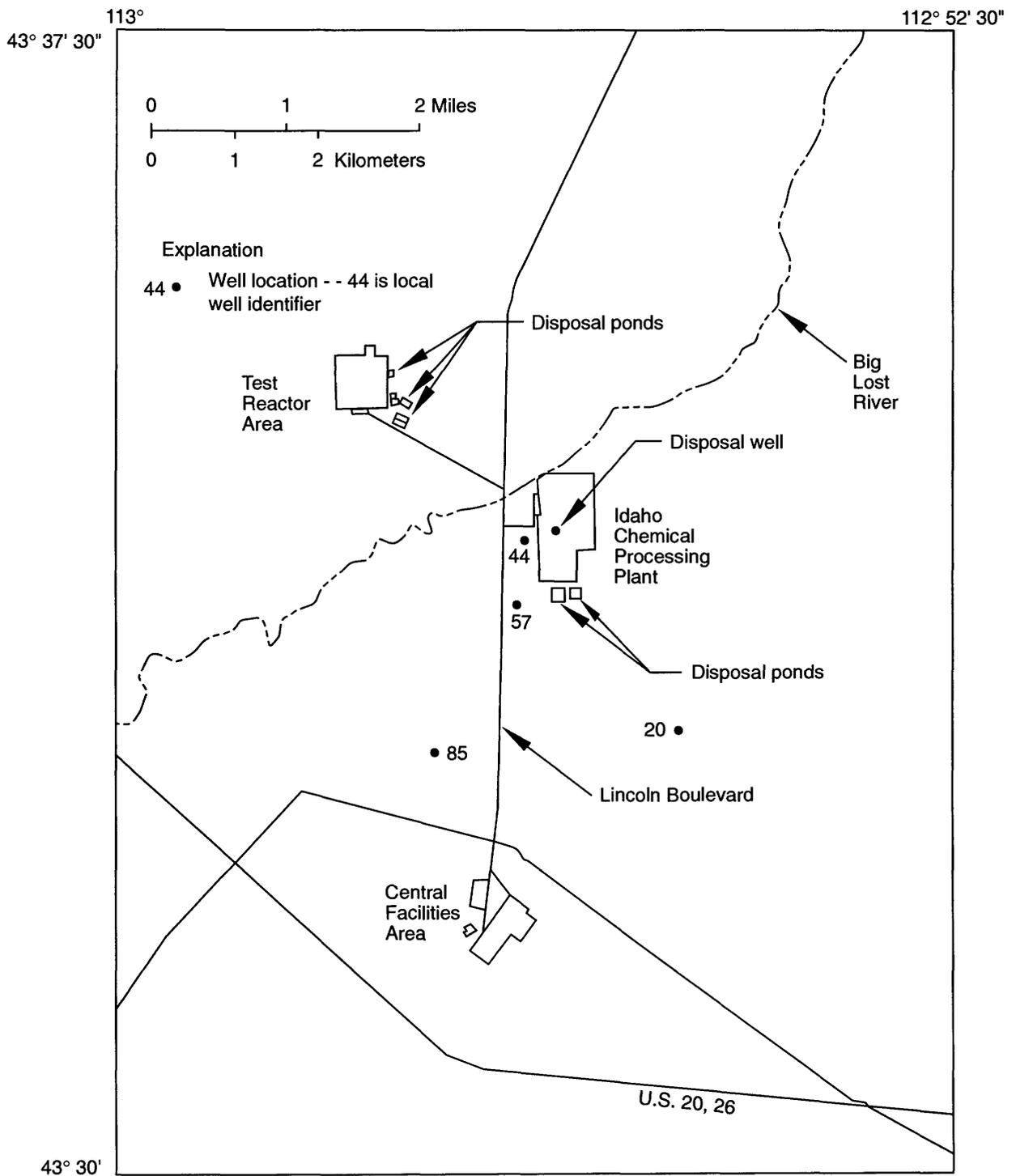


Figure 2. Location of observation wells completed in the Snake River Plain aquifer, the wastewater-disposal well, and disposal ponds near the Idaho Chemical Processing Plant and the Test Reactor Area.

Historically, the distribution of  $^3\text{H}$  has been used to define the extent that the Snake River Plain aquifer has been influenced by wastewater-disposal practices (Duffy and Harrison, 1987). However, the 12.43 year half-life of  $^3\text{H}$  and the detection capability (18.5 Bq/L) that is used at the INEEL for routine monitoring limit the utility of this radionuclide for hydrologic studies. Prior to 1990, concentrations of  $^{36}\text{Cl}$  (half-life is 301,000 years) at the INEEL were determined by beta-counting methods (BCM) and  $^{129}\text{I}$  (half-life is 15.7 million years) concentrations were determined by neutron activation analysis (NAA). Ground-water samples analyzed by accelerator mass spectrometry (AMS) in 1990 and 1991 contained concentrations of  $^{36}\text{Cl}$  and  $^{129}\text{I}$  that previously were not detectable; therefore, a more accurate description of the area influenced by wastewater disposal can be made because the analytical method detection limit for AMS is several orders of magnitude lower than that for either BCM or NAA.

Since 1966, the USGS routinely has archived at least one suite of quarterly ground- and surface-water samples each year. The samples and a large associated geochemical database are available for research purposes. These archived samples, the chemical database, and the capability to detect radionuclides such as  $^{36}\text{Cl}$  at small environmental concentrations by AMS may allow determination of historical trends in radionuclide concentrations, historical development of the waste chlorine plume, and large-scale aquifer hydrogeologic properties such as ground-water flow velocities and dispersion.

The basis for the research reported here is the evaluation of potential waste transport using the existing database combined with new chlorine isotope data generated from reanalyzing the archived ground- and surface-water samples. These data will be used to reconstruct the historical development of the waste chlorine plume in the Snake River Plain aquifer with particular emphasis on  $^{36}\text{Cl}$ . Reconstruction should permit the definition of first arrival times of wastewater containing  $^{36}\text{Cl}$  at monitoring wells downgradient from the ICPP with more confidence and accuracy than has been reported for investigations involving the use of disposed  $^3\text{H}$  as a tracer. Reconstruction

also should permit definition of the development of the plume front (in at least two dimensions) and thereby establish longitudinal and transverse dispersivities from the waste plume.

## **Purpose and Scope**

The purpose of this report is to describe the evaluation of water samples from the USGS archive library in terms of chlorine isotope fractionation and thereby establish confidence in utilizing chloride isotopic data for these water samples. The evaluation covered the period of archived samples available for selected sites at the INEEL and included: (1) assessment of paper and computer records for each sample, (2) determination of stable chlorine ratios in the water samples, and (3) determination of  $^{36}\text{Cl}$  and dissolved chloride concentrations in the water samples. These assessments and analyses were performed to ascertain if chlorine isotope fractionation may have occurred during storage. This information is essential in determining the suitability of using  $^{36}\text{Cl}$  concentrations in the archived water samples to reconstruct the wastewater plume through time and space. The scope of this report was limited to the evaluation of archived water samples from six USGS monitoring wells from 1966-93 and one surface-water site for 1970.

## **Previous Investigations**

Many investigators have described the geology and hydrology of the Snake River Plain at the INEEL in a continuing series of reports published by the USGS. Robertson and others (1974) described the regional hydrogeology and the influence of wastewater disposal on ground-water geochemistry for 1952-70, Barraclough and Jensen (1976) described hydrologic conditions during 1971-73, Barraclough and others (1982) for 1974-78, Lewis and Jensen (1985) for 1979-81, Pittman and others (1988) for 1982-85, Orr and Cecil (1991) for 1986-88, and Bartholomay and others (1995) for 1989-91. Cecil and others (1991) also described the hydrogeology and influence of wastewater disposal in perched ground-water zones for 1986-88.

Several studies also have been made to digitally model waste plumes in the fractured

basalt. Robertson (1974) was the first to describe the construction of a computer model to represent the transport of radioactive and chemical wastes in the Snake River Plain aquifer at the INEEL. Robertson calibrated a two-dimensional flow and transport model using data from the USGS for 1952–70 and predicted solute spreading in the Snake River Plain aquifer at the INEEL to the year 2000. The calibrated longitudinal ( $\alpha_L$ ) and transverse ( $\alpha_T$ ) dispersivities were about 90 and 140 m respectively. This characteristic,  $\alpha_T > \alpha_L$ , is not expected theoretically and is still unique among field-scale investigations. Gelhar and others (1992) critically reviewed investigations of 59 different sites on field-scale dispersion in aquifers and found that for 24 values of horizontal transverse dispersivities reported, all but those by Robertson were one to two orders of magnitude less than longitudinal values. Subsequent reevaluation of Robertson's work and new attempts at modeling flow and transport at the INEEL have not resolved this apparent discrepancy (Duffy and Harrison, 1987; Fryar and Domenico, 1989; and Goode and Konikow, 1990). Although an evaluation of sampling and preservation methods for strontium-90 has been performed at the INEEL (Cecil and others, 1989), no previous investigations on variations in stable chlorine isotopic ratios have been reported for the eastern Snake River Plain aquifer.

## Acknowledgments

The authors thank Dr. Pankaj Sharma, formerly at the University of Rochester and now at Purdue University, for his assistance and advice on quality assurance/quality control samples for  $^{36}\text{Cl}$  analyses. The authors also thank Drs. Gwen Milton and Jack Cornett of Chalk River Laboratory in Ontario, Canada, for their assistance on  $^{36}\text{Cl}$  quality assurance/quality control samples. The authors also thank Laurie Wirt and John A. Isbicki of the USGS for their critical review of this report.

## CHLORINE ISOTOPES

Fifteen isotopes of chlorine (Cl) are known to exist; 2 are stable and 13 are radioactive. Of the stable isotopes, chlorine-35 ( $^{35}\text{Cl}$ ) is the most common in nature with 75.77-percent abundance

and an atomic weight of 34.9689 g (CRC Handbook, 1991). The other stable isotope,  $^{37}\text{Cl}$ , has an abundance in nature of 24.23 percent and an atomic weight of 36.9659 g. Of the 13 radioactive isotopes, only  $^{36}\text{Cl}$  has a half-life greater than 1 hour; the half-life for  $^{36}\text{Cl}$  is 301,000 years (Walker and others, 1989). Several oxidation states for chlorine isotopes are found in nature but with a few rare exceptions, the -I oxidation state as the chloride ion is dominant. Oxidation states of +VII for perchlorates ( $\text{ClO}_4^-$ ) and +I for hypochlorites ( $\text{HOCl}$ ) have been reported (Erickson, 1981; Sienko and Plane, 1966).

Actual isotopic ratio measurements of elements are difficult to perform because variations in isotopic composition are small. Therefore, the isotopic ratio of  $^{37}\text{Cl}/^{35}\text{Cl}$  is measured relative to the same ratio in a standard sample and expressed in the delta ( $\delta$ ) permil notation defined as:

$$\delta^{37}\text{Cl} = \left( \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) 1000$$

where

$R_{\text{sample}}$  = ratio of  $^{37}\text{Cl}/^{35}\text{Cl}$  in the sample, and

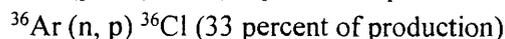
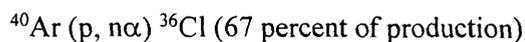
$R_{\text{standard}}$  = ratio of  $^{37}\text{Cl}/^{35}\text{Cl}$  in the standard

Variations in  $\delta^{37}\text{Cl}$  in ground water may be a result of diffusion, ion-filtration, mixing, dissolution of evaporites along a flow path, and/or temperature and pressure effects in geothermal systems. Diffusion has been proven to be a process that causes significant variations in chlorine isotopic ratios (Desaulniers and others, 1986). Additionally, Eggenkamp (1994) showed significant  $\delta^{37}\text{Cl}$  variations in geothermal water and possible significant variations through diffusion modeling. None of these processes are expected to be an effective means of fractionation of chlorine isotopes in water from the eastern Snake River Plain aquifer because: (1) diffusion is unlikely with ground-water flow velocities ranging from 1.5 to 6 m/day (Robertson and others, 1974); (2) there are no significant ion-filtration processes operable along the flowpath such as large-scale ground-water flow through clay beds; (3) regional ground-water mixing is minimal; (4) there are no significant deposits of evaporites along the flowpath from recharge to discharge; and (5) geothermal effects are minimal. Additionally, the archived samples have been in temperature-controlled storage since

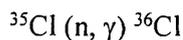
the date of sample collection. Measurements of  $\delta^{37}\text{Cl}$  were made on selected samples to document possible variations through time and to ensure that  $^{36}\text{Cl}$  concentrations measured in the 1990's, for water samples collected in the 1960–80's, were representative of the concentration at the time of sample collection.

The internationally accepted standard for  $\delta^{37}\text{Cl}$  is Standard Mean Ocean Chloride (SMOC) as described by Kaufmann and others (1984); the ratio of  $^{37}\text{Cl}/^{35}\text{Cl}$  was shown to be constant in 15 samples worldwide. The standard for this study was collected near Fairfax, Nova Scotia and was compared with measurements performed on the same standard at the University of Arizona. The measured  $\delta^{37}\text{Cl}$  SMOC for the sample collected near Fairfax, Nova Scotia was  $0.00 \pm 0.18$  permil. For comparison, our  $\delta^{37}\text{Cl}$  measurements for samples collected from the Gulf of Mexico and the Baltic Sea were  $-0.13 \pm 0.19$  and  $-0.21 \pm 0.11$  permil, respectively. These results are statistically the same as our result for the sample collected near Fairfax, Nova Scotia.

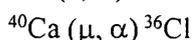
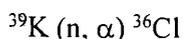
Chlorine-36, a beta-particle emitter, is cosmogenically produced in the atmosphere by two major processes: (1) spallation (cosmic-ray interaction with argon-40 ( $^{40}\text{Ar}$ )); and (2) neutron activation of  $^{36}\text{Ar}$  according to the following reactions (Andrews and Fontes, 1992):



Another significant source of  $^{36}\text{Cl}$  in the environment is the neutron activation of stable  $^{35}\text{Cl}$ :



This reaction is the source of  $^{36}\text{Cl}$  produced during atmospheric weapons tests conducted by the United States over the Pacific Ocean during 1952–58 (Schaeffer and others, 1960). This reaction may also produce significant  $^{36}\text{Cl}$  in situ in certain subsurface environments that have a neutron source in reasonably close proximity to stable chlorine. In basalt, sandstone, and carbonate rocks the following reactions can contribute to in-situ production:



Factors that determine in-situ production include: (1) content of Cl, potassium (K), Ar, and calcium (Ca) in the rocks; (2) proximity of these elements to a source of incident particles to initiate the nuclear reactions; and (3) irradiation time of the target nuclides.

There are three potential sources for  $^{36}\text{Cl}$  in ground water. These are, (1) meteoric input of cosmogenically produced  $^{36}\text{Cl}$  through wet and dry deposition and recharge; (2) in-situ production between nuclear particles and stable elements; and (3) anthropogenic sources such as fallout from atmospheric weapons tests and emissions from nuclear reactor facilities.

Bentley and others (1986) predicted pre-weapons test  $^{36}\text{Cl}/\text{Cl}$  ratios for the continental United States. These predictions are based on long-term deposition of both wet and dry precipitation and represent integrated ratios expected for ground water that has not been exposed to anthropogenic or significant in-situ produced  $^{36}\text{Cl}$ . This box model assumes that evapotranspiration processes increase the absolute concentration of chloride isotopes in ground water but do not affect meteorically-derived isotope ratios. In many ground-water environments, the chloride concentration increases along a flow path and the meteoric input of  $^{36}\text{Cl}$  may be diluted by the addition of chloride from the aquifer matrix or from the unsaturated zone that recharge must travel through. This type of total chloride would have a  $^{36}\text{Cl}/\text{Cl}$  ratio that is in equilibrium with the in-situ activated stable  $^{35}\text{Cl}$  and would not fit the model postulated by Bentley and others.

Bentley and others (1986) predicted that spallation of  $^{40}\text{Ar}$  produces a global  $^{36}\text{Cl}$  fallout of 11 atoms/ $\text{m}^2/\text{sec}$  and neutron activation of  $^{36}\text{Ar}$  produces 5 atoms/ $\text{m}^2/\text{sec}$ . However, Hossain (1988) published new data on the capture cross section of the  $^{36}\text{Ar} (n, p) ^{36}\text{Cl}$  reaction that indicate the probability of this reaction is reduced to less than 1.5 millibarns as opposed to 1.83 barns as was used for the calculations of Bentley and others. This complicating factor was pointed out by Andrews and Fontes (1992, p. 247). They suggest that the global fallout values used in this box model should be reduced by 11/16 because neutron activation of  $^{36}\text{Ar}$  appears to be an insignificant

meteoric source. This apparent reduction of the significance of neutron activation of  $^{36}\text{Ar}$  is important to establishing pre-bomb  $^{36}\text{Cl}/\text{Cl}$  ratios because the values in the model are modified by prevailing winds and orographic effects as one moves away from coastal to continental areas and latitudinal variations. It is the latitudinal variations that are most affected by the differences in the probability of the neutron activation of  $^{36}\text{Ar}$ . Another even more complicating factor in attempting to determine the meteoric input function is the fact that calculations of the  $^{36}\text{Cl}$  content of an ice core from Greenland, designated the Dye 3 site, show that the fallout rate from  $^{40}\text{Ar}$  spallation is larger than the value originally calculated by Lal and Peters (1967).

Chlorine-36 can be produced at detectable concentrations in both the deep and shallow subsurface. In the deep subsurface, neutron activation of  $^{35}\text{Cl}$  and  $^{39}\text{K}$  is the dominant source for the production of  $^{36}\text{Cl}$ . The neutrons required for these reactions are produced by the interaction between  $\alpha$ -particles, generated from the radioactive decay of uranium and thorium series isotopes, and stable nuclei of lighter elements such as fluorine, oxygen, sodium, aluminum, and silica (Faure, 1986). An estimate can be made of in-situ produced  $^{36}\text{Cl}$  for a given ground-water system if the following contributing factors are known: (1) the U and Th content of the aquifer matrix; (2) the total chloride content of both the aquifer matrix and the water in the aquifer; (3) the irradiation time of the target nuclei; and (4) proximity of targets to neutrons. Andrews and others (1989) made such calculations for  $^{36}\text{Cl}$  production in the Stripa granite. Using the Stripa study as a model, Beasley and others (1993) calculated a theoretical in-situ produced  $^{36}\text{Cl}/\text{Cl}$  ratio of  $1 \times 10^{-18}$  for the basalt aquifer of the eastern Snake River Plain in southeastern Idaho. This ratio is not measurable even with AMS and in-situ production was determined to be inconsequential.

Thermonuclear explosions conducted in the atmosphere over the Earth's oceans produced levels of  $^{36}\text{Cl}$  that exceeded natural production by three orders of magnitude at Long Island, New York (Bentley and others, 1982). This pulse is analogous to bomb-produced  $^3\text{H}$  and can be used to trace and date recent ground water or determine net

water infiltration rates through the unsaturated zone in semi-arid areas. Peak bomb production of  $^{36}\text{Cl}$  was in 1958 and Bentley and others (1986) modeled the fallout using data from a series of nuclear tests conducted during 1952–58.

The use of bomb-produced  $^3\text{H}$  to identify water introduced into the hydrologic cycle during 1955–70 has become common practice. A review of studies of this type would be a major undertaking and is beyond the scope of this report. As early as 1957, Begemann and Libby (1957) recognized the importance of  $^3\text{H}$  input to the hydrologic environment as a result of weapons tests. However, this bomb pulse of  $^3\text{H}$  is only a temporary tool to hydrogeologists due to the relatively short half-life of 12.43 years.

Chlorine-36, on the other hand, is a conservative tracing tool available with similar attributes as  $^3\text{H}$  but has a much longer half-life. Neutron activation of  $^{35}\text{Cl}$  is the major production mechanism for  $^{36}\text{Cl}$  during nuclear explosions although minor amounts are produced by fission and activation of  $^{36}\text{Ar}$ . Advantages of using  $^{36}\text{Cl}$  over  $^3\text{H}$  in these kinds of studies include: (1)  $^{36}\text{Cl}$  was produced by a limited number of tests between 1952–58 over oceans; (2)  $^{36}\text{Cl}$  was washed out of the atmosphere relatively rapidly as opposed to bomb-produced  $^3\text{H}$ ; and (3) the weapons tests that produced  $^{36}\text{Cl}$  were concentrated around the equator and global fallout was symmetrical in both hemispheres, whereas  $^3\text{H}$  fallout was predominately in the northern hemisphere due to the location of the tests that produced it.

## GEOHYDROLOGIC SETTING

The stratigraphy at the INEEL consists of layered sequences of basaltic-lava flows and cinder beds with interbedded sediments mainly made up of fluvial and lacustrine deposits. Individual lava flows typically are 6 to 7.5 m thick and 130 to 260 km<sup>2</sup> in areal extent providing potential for relatively large regional aquifer systems within individual volcanic-extrusive episodes. Rubble, clinker zones, fractures, and vesicular zones are prevalent near the surfaces of lava flows and may serve as preferential pathways for ground-water movement. Subsequent lava flows or sedimentary deposits may partly fill fractures and vesicles and

thereby restrict ground-water flow. The centers of individual flows, especially thick flows, are typically less vesicular and more massive and may be characterized by vertical fractures further complicating the interpretation of the ground-water flow system.

The geology and hydrology of the Snake River Plain at the INEEL describe a water-table aquifer of large areal extent with overlying perched aquifers near waste-disposal ponds (Cecil and others, 1991). Regional ground-water flow is from the northeast to the southwest. Perched aquifers form when downward flow from waste ponds is impeded by silt and clay in sedimentary deposits or by dense sections at the interiors of basalt flows. Well yields are large because of the highly transmissive nature of the fractured, vesicular interflow zones. The aquifer framework results in a complex, heterogeneous, and anisotropic medium.

The water table for the Snake River Plain aquifer at the INEEL ranges from about 60 m below land surface in the north-central part to about 270 m in the southeastern part. Ground-water levels have been relatively stable over the last 45 years, although they respond to climatic trends and, locally, to recharge from intermittent streams. Perched water tables are usually between 15 and 40 m below land surface. Hydrologic conditions for perched aquifers are documented in Cecil and others (1991).

Estimated linear ground-water flow velocities in the eastern Snake River Plain aquifer range from about 1.5 to 6 m/day with an average of 3 m/day (Robertson and others, 1974). Recent tracer studies with  $^3\text{H}$  indicate that wastewater from the ICPP was detected in wells at the southern boundary of the INEEL in 1983 (Mann and Cecil, 1990). This represents contaminant movement of about 13 km in 30 years for an approximate minimum linear flow velocity of 1.2 m/day or slightly lower than the range reported by Robertson and others (1974). Iodine-129 was detected in well USGS 11 at a concentration above background in 1991, representing a linear-flow velocity of 1.8 m/day (Mann and Beasley, 1994). Data presented in this evaluation of the archived water samples indicates the  $^{36}\text{Cl}$  from INEEL operations was detectable at well USGS 14 no later than 1982 (table 2); the

minimum velocity calculated from this estimate of first arrival is 2.4 m/day. The  $^{36}\text{Cl}$  concentration in water from well USGS 14 in 1982 was  $3.1 \pm 0.3 \times 10^8$  atoms/L or about 3 times the estimated background (including weapons-test contributions) reported for the eastern Snake River Plain aquifer (Cecil and Vogt, 1997). These relatively large linear minimum velocities from recent tracer studies, 1.2 to 2.4 m/day over large distances, suggest that ground water and solutes move on a regional scale predominantly by advection with no apparent diffusion or ion-filtration that could cause fractionation of chloride isotopes.

## METHODS

The following sections describe field and analytical methods and quality assurance practices used for this evaluation. Beginning in September 1987, field conditions at each site were documented and a chain-of-custody record was maintained from the time of sample collection until the sample was delivered to the laboratory. Prior to September 1987, field notes and original laboratory data sheets were maintained for each sample. The field books, notes, laboratory data sheets, and chain-of-custody records are available for inspection at the USGS's INEEL Project Office.

### Field Methods

Water samples from the Snake River Plain aquifer were selected from the USGS sample-archive library for six sites near and downgradient from the ICPP (fig. 1 and table 1) and were analyzed for  $\delta^{37}\text{Cl}$ ,  $^{36}\text{Cl}$ , and dissolved chloride. At the time of collection, two methods were used to obtain water from the wells. If a well was equipped with a dedicated submersible or turbine pump, the well was pumped and the samples were collected at the end of the discharge pipe or at a spigot in the discharge pipe. A remotely operated thief sampler was used to obtain a water sample from ground-water monitoring wells not equipped with dedicated pumps. Since sampling for ground water began in the 1950's, the proportion of wells with dedicated pumps has increased significantly. From the 1950's to the mid 1980's, thief samplers were used to collect most water samples. By the late

1980's, most wells were equipped with dedicated pumps.

Wells equipped with dedicated submersible or turbine pumps were pumped until temperature, pH, and specific conductance measurements stabilized as described by Wood (1981) and Claassen (1982). A water sample was then collected provided an ample volume of water had been pumped from the well. At most wells, a volume of water equivalent to a minimum of 3 wellbore volumes was pumped from each well; at many wells, 5 to 10 wellbore volumes were pumped prior to the collection of a sample.

For wells without dedicated pumps, a thief sampler was lowered inside the well casing to a predetermined level. The thief sampler is constructed in such a manner that water passes through the sampler while it is being lowered to the sampling level. Once at the sampling level, the ends of the sampler are closed, trapping about 1 liter of water.

Based on drillers' geophysical and fluid-conductivity logs, fracture zones have been

identified in the basaltic rocks opposite perforations in the casing or in open intervals. The relation between ground-water circulation, specific conductance, and well construction for well USGS 28 is illustrated in figure 3. Water likely moves through the fracture zones at a high velocity when compared with the velocity in unfractured zones; between about 77-83 meters below land surface for USGS 28 (fig. 3). Each thief sample for all wells was collected at predetermined levels to obtain samples that represented water moving through the aquifer rather than water that may have stagnated in the wellbore and casing opposite unfractured zones. The thief sampler was cleaned and rinsed with a pressurized spray of deionized water prior to and after use at each well.

### Analytical Methods

Dissolved chloride analyses were performed by three laboratories: DOE's Radiological and Environmental Sciences Laboratory (RESL), the University of Waterloo's Environmental Isotope Laboratory (UWIL), and the USGS's National Water Quality Laboratory (NWQL). Methods of

**Table 1.** Archived ground-water samples collected from selected wells for chloride isotopic analyses [See Figure 1 for well locations. T, indicates thief sample; P, indicates pumped sample]

Well identifier	Total depth and interval of well perforated or open to aquifer (meters)	Type of sample	Sample depth (meters)	Depth to water (meters)	Date depth to water measured	Date depth to water sampled
USGS 14	226/216-225	T	222	215	04/15/82	04/15/82
		T	222	214	04/08/87	04/08/87
		P	222	215	04/16/93	04/16/93
USGS 19	120/86-92	T	87	80	10/28/69	10/28/69
		T	89	78	04/28/83	04/08/83
		P	97	83	04/07/93	04/07/93
USGS 20	203/140-143 155-166	T	159	137	04/28/69	04/28/69
		T	159	138	04/29/83	04/12/83
		P	150	137	04/04/88	04/04/88
		P	156	139	04/14/93	04/14/93
USGS 44	195/138-195	T	150	136	08/05/69	05/08/69
		T	150	137	08/01/83	04/12/83
		T	150	137	04/09/88	04/09/88
		P	150	139	05/04/93	05/04/93
USGGS 57	220/143-220	T	162	138	08/05/69	05/08/69
		T	165	140	08/01/83	04/12/83
		P	152	138	03/31/88	03/31/88
		P	152	140	04/15/93	04/15/93
USGS 85	191/157-191	T	171	144	04/25/69	04/25/69
		T	171	144	04/28/83	04/13/83
		P	157	146	04/19/93	04/19/93

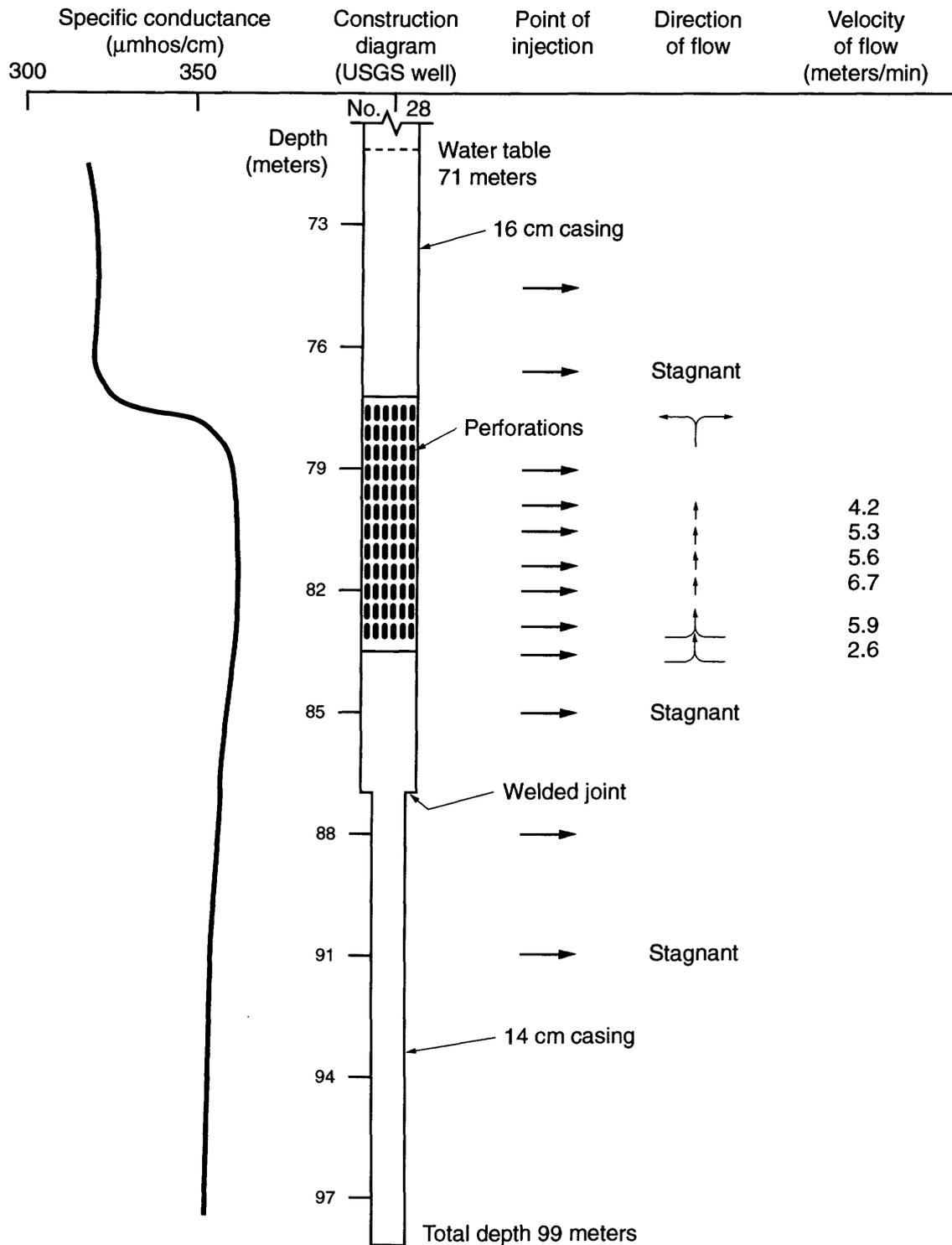


Figure 3. Relation of ground-water movement, specific conductance, and well construction for well USGS 28 (modified from Morris and others, 1964).

chloride determination included: (1) silver nitrate titration (American Society for Testing and Materials (ASTM), 1982); (2) ion-selective electrode (ASTM, 1982); and (3) ion chromatography (Fishman and Friedman, 1989). RESL performed all analyses listed in table 2 for dissolved chloride at date of sample collection. For samples collected prior to May 1975, the method used was a silver-nitrate titration. Using this method, a water sample was adjusted to a pH of 8.3 and then titrated in the presence of potassium chromate indicator solution. The end point in the titration was indicated by a red-brick colored silver chromate solution. The ion-selective electrode method was used for those analyses performed for chloride after May 1975. Using this method, the chloride-ion concentration is determined potentiometrically with a chloride ion-selective electrode in tandem with a double-junction, sleeve-type reference electrode. Potentials were then read with either a selective-ion meter with a concentration scale for chloride or a pH meter with an expanded millivolt scale. The electrodes were calibrated to traceable standards.

The chloride analyses in table 2 performed by UWIL and the NWQL were determined by the ion chromatography method. A standard two-column ion chromatography technique was employed by both labs. Water samples were placed in a liquid mobile phase (eluent) and pumped at a constant flow rate through two ion-exchange columns in tandem. Chloride ions were separated from solution in the first column based on their affinity for exchange sites on an anion-specific resin. The second column decreased the background conductivity of the eluent to a minimal level to suppress interference. Separated chloride ions then were quantified with a specific-conductance cell and an anion chromatogram was produced.

Until 1977,  $^{36}\text{Cl}$  in environmental samples was measured by counting beta-particle emissions during radioactive decay. These kinds of measurements were difficult due to the relatively long half-life of 301,000 years and the resultant small specific activity of  $^{36}\text{Cl}$ . Muller (1977) postulated that by using particle accelerators as mass spectrometers, radionuclides with relatively long half-lives (such as carbon-14 ( $^{14}\text{C}$ ) and

beryllium-10 ( $^{10}\text{Be}$ )) could be measured at environmental concentrations. Later in 1977, AMS measurements of  $^{14}\text{C}$  were reported by McMaster University in Canada and the University of Rochester in the United States. In 1979, the first successful measurements of  $^{36}\text{Cl}$  in ground-water samples were carried out at the University of Rochester on a tandem Van De Graaf accelerator system. The first such use of accelerators was for helium-3 measurements in 1939 by Alvarez and Cornog (Elmore and others, 1979). Since 1979, thousands of environmental samples have been measured for their  $^{36}\text{Cl}$  content at more than 20 accelerator facilities worldwide.

With conventional decay counting methods, tens of grams of chloride were required and counting times as long as a week were common. With AMS, sample size has been reduced to as little as 1.0 mg total chloride and counting times of 30 minutes with 10 percent precision. Sensitivity has also improved with AMS; beta counting methods have a sensitivity of about one  $^{36}\text{Cl}$  atom in  $10^{12}$  chlorine atoms and AMS methods have a sensitivity of about 5 atoms of  $^{36}\text{Cl}$  in  $10^{15}$  chlorine atoms. This AMS sensitivity corresponds to about one beta-particle emission per year and is not detectable by scintillation counting.

AMS operates the same as conventional mass spectrometry by using the fact that all charged atomic and molecular species have unique masses. Just as in mass spectrometry, AMS is made up of four steps: (1) formation of a charged atomic or molecular species; (2) acceleration of this species through an electrostatic potential (ES); (3) separation of ions based on their mass-to-charge ratios; and (4) determination of the number of ions or atoms in a detector system. With AMS, acceleration is through ES of megavolt (MeV) energies in contrast to ES of kilovolt energies found in conventional mass spectrometry. Because particle accelerators operate at high energies, molecular ions are removed from the analytical line by gas-filled magnets; only target atoms (or atoms of the same mass as the target, that is interfering atoms) remain at the detectors (Elmore and Phillips, 1987). In the case of  $^{36}\text{Cl}$ , interference from isobars is removed by selecting charge

**Table 2.** Stable chlorine isotope results, dissolved chloride, and chloride-36 concentrations for archived ground-water samples collected from selected wells and the Little Lost River, Idaho National Engineering and Environmental Laboratory, Idaho

[ $\delta^{37}\text{Cl}$ , indicates delta chloride-37, see text for explanation of uncertainties; Cl, indicates dissolved chloride;  $^{36}\text{Cl}$ , indicates chloride-36; NA, indicates not applicable; R, analyses performed by Radiological and Environmental Sciences Laboratory; W, analyses performed by University of Waterloo Environmental Isotope Laboratory; N, analyses performed by USGS's National Water Quality Laboratory; P, analyses performed by Purdue University's PRIME Laboratory; NR, indicates blind replicate analyzed by the USGS's National Water Quality Laboratory; CRL, indicates blind replicate analyzed by Chalk River Laboratory. Symbol: --, indicates no data available; \*, indicates uncertainties estimated using equation 3 in text.]

Site identifier	Date sampled	$\delta^{37}\text{Cl}$ $\pm 0.2$ permil unless noted	Dissolved Cl at date sampled (mg/L)	Dissolved Cl in 1993 (mg/L) $\pm 10$ percent unless noted	In Situ ( $^{36}\text{Cl}/\text{Cl}$ ) $\times 10^{-13}$	$^{36}\text{Cl}$ (atoms/L) $\times 10^8$
USGS 14	04/15/82	+0.47 $\pm$ 0.01	25 $\pm$ 2*R	21.4 W	7.41 $\pm$ 0.58P	3.1 $\pm$ 0.3
	04/08/87	-0.44 $\pm$ 0.5	21 $\pm$ 2*R	28.4 W	52.5 $\pm$ 0.5P	19 $\pm$ 0.2
	10/01/93	+0.20	NA	18 $\pm$ 1 *N	17.4 $\pm$ 0.9P	5.3 $\pm$ 0.3
	10/01/93	--	--	21 $\pm$ 1 *NR	--	--
USGS 19	10/20/69	+0.12	--	29.0 W	5.8 $\pm$ 0.6P	2.9 $\pm$ 0.3
	10/20/69	--	--	--	7.0 $\pm$ 0.7CR	3.5 $\pm$ 0.4
	04/08/83	+0.10	21 $\pm$ 1*R	14.9 W	14.1 $\pm$ 0.9P	2.4 $\pm$ 0.2
	10/01/93	+0.02	NA	11 $\pm$ 0.7 *N	5.7 $\pm$ 0.3P	1.1 $\pm$ 0.1
	10/01/93	--	--	11 $\pm$ 0.7*NR	--	--
USGS 20	04/28/69	+0.26	30 $\pm$ 3*R	30.7 W	5,030 $\pm$ 200P	2,600 $\pm$ 100
	04/12/83	+0.01	24 $\pm$ 2*R	21.6 W	6,430 $\pm$ 300P	2,600 $\pm$ 130
	04/04/88	+0.41	24 $\pm$ 2*R	28.2 W	8,150 $\pm$ 200P	3,300 $\pm$ 82
	10/19/93	+0.34	NA	23 $\pm$ 1 *N	9,000 $\pm$ 270P	3,500 $\pm$ 100
USGS 44	05/08/69	+0.21	12 $\pm$ 1*R	10.6 W	215 $\pm$ 40P	44 $\pm$ 8
	04/12/83	+0.19 $\pm$ 0.15	59 $\pm$ 6*R	52.8 W	553 $\pm$ 200P	5,500 $\pm$ 200
	04/09/88	+0.11	15 $\pm$ 2*R	17.0 W	541 $\pm$ 20P	140 $\pm$ 5
	11/01/93	+0.42	NA	20 $\pm$ 1 *N	580 $\pm$ 42P	200 $\pm$ 14
	11/01/93	--	--	19 $\pm$ 1 *NR	--	--
USGS 57	05/08/69	-0.13 $\pm$ 0.1	50 $\pm$ 5*R	46.9 W	21,000 $\pm$ 580P	18,000 $\pm$ 490
	04/12/83	+0.59 $\pm$ 0.16	127 $\pm$ 13*R	112 W	10,000 $\pm$ 400P	22,000 $\pm$ 860
	03/31/88	-0.12 $\pm$ 0.01	67 $\pm$ 7*R	69.2 W	19,300 $\pm$ 640P	28,000 $\pm$ 910
	10/12/93	+0.09	NA	180 $\pm$ 7 *N	5,600 $\pm$ 120P	17,000 $\pm$ 360
	10/12/93	--	--	190 $\pm$ 8 *NR	--	--
USGS 85	04/25/69	+0.12	24 $\pm$ 2*R	21.3 W	14,800 $\pm$ 400P	6,000 $\pm$ 160
	04/13/83	+0.21	37 $\pm$ 4*R	33.8 W	8,460 $\pm$ 200P	5,300 $\pm$ 130
	11/04/93	-0.05	NA	74 $\pm$ 3 *N	2,400 $\pm$ 270P	3,000 $\pm$ 34
	11/04/93	--	--	73 $\pm$ 3 *NR	--	--
Little Lost River (13119000)	04/03/70	+0.27 $\pm$ 0.23	--	13 W	--	--

states that have no common factor with 36, for example, charge states 5, 7, 11, 13, or 17. Because the most common interference for  $^{36}\text{Cl}$  measurements is from sulfur-36 ( $^{36}\text{S}$ ), elimination of sulfate from water samples and selection of the correct charge state for analyses are crucial to obtaining meaningful results. Sulfate in ground water at the INEEL is a potential interference problem for  $^{36}\text{Cl}$  analyses. Sulfate concentrations in 66 ground-water samples collected in October 1995 at the INEEL ranged from 11 to 230 mg/L (Bartholomay, USGS, written commun., 1996). These concentrations are representative of ground water at the INEEL since monitoring operations started in 1953. Therefore, sulfate was removed from the water samples used in this study as outlined later in the methods section.

Water samples from the sample archive library were analyzed for  $^{36}\text{Cl}$  using Tandem Accelerator Mass Spectrometry (TAMS) at PRIME Laboratory, Purdue University. The PRIME TAMS facility is based on an upgraded 8-million volt tandem accelerator with a high intensity ion source, a 150-thousand volt (kV) ion-source injector, and a beam line and detector system. The 150 kV ion source is a cesium gun used to sputter chloride ions from a silver chloride ( $\text{AgCl}$ ) target. The negative ions are focused and passed through a  $90^\circ$  inflection magnet and accelerated toward a fixed positive potential at the tandem accelerator. At the entrance to the tandem accelerator, the negative ions pass through carbon foil that strips off valence electrons and molecular species. The resultant beam of positive ions are accelerated away from the positive terminal toward ground potential and a series of mass/charge analyzers and a gas-ionization detector.

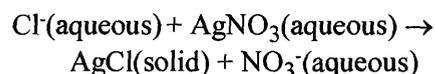
The chloride isotope laboratory at the University of Waterloo was used to prepare the samples for TAMS analysis. Sample preparation for  $^{36}\text{Cl}$  analysis includes preconcentration of Cl in solution, precipitation of  $\text{AgCl}$ , and purification of the  $\text{AgCl}$  target. As previously mentioned, because  $^{36}\text{S}$  is an interfering isobar, care must be taken to

remove as much sulfate from the water sample as possible.

Before using the chlorine isotope laboratory at the University of Waterloo for TAMS target preparation, a laboratory swipe was taken from the counter tops and overhead lamps on January 7, 1993. Approximately 1.2 g of material were dissolved in 20 mL of 18 Mohm deionized water. This solution was analyzed for Cl at the UWIL and for  $^{36}\text{Cl}$  at the University of Rochester Nuclear Structures Research Laboratory (NSRL). The results are presented in table 3. Subsequent to receiving the results of the first lab swipe, all surfaces in the chlorine lab were cleaned with an Alconox soap solution, followed by a 2-percent ultrapure nitric-acid ( $\text{HNO}_3$ ) solution with a final rinse with 18 Mohm deionized water. A second lab swipe was done on April 15, 1993, and approximately 0.2 g of material were dissolved in 20 mL of 18 Mohm deionized water. The swipe taken after cleaning the laboratory was analyzed for Cl at UWIL and for  $^{36}\text{Cl}$  at NSRL and at PRIME laboratory (table 3). The results of the dissolved Cl and  $^{36}\text{Cl}$  analyses showed a reduction in Cl concentration from  $282 \pm 28$  to  $10 \pm 1$  mg/L and a reduction in  $^{36}\text{Cl}/\text{Cl}$  from  $263 \pm 21 \times 10^{-15}$  to  $5 \pm 10 \times 10^{-15}$  (table 3). The laboratory at UWIL was then ready to be used to prepare  $\text{AgCl}$  targets for  $^{36}\text{Cl}$  analyses.

The first step in sample preparation for  $^{36}\text{Cl}$  analysis is normally preconcentration of Cl. Because all samples in this study contained a minimum of  $10.6 \pm 1.1$  mg/L of Cl, well USGS 44, (table 2), it was determined that no preconcentration was necessary to ensure 8 to 10 mg of  $\text{AgCl}$  for a target. The next steps in preparing targets for TAMS measurements were precipitation and purification of  $\text{AgCl}$  (Conrad and others, 1986).

Samples were acidified to pH 2 using ultrapure  $\text{HNO}_3$ . Chloride was then precipitated from the acidified samples as  $\text{AgCl}$  by the addition of 15 mL of 0.1 molar (M) ultrapure silver nitrate ( $\text{AgNO}_3$ ).

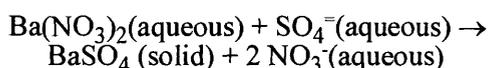


**Table 3.** Results of laboratory swipes taken at the University of Waterloo Isotope Laboratory before and after clean-up [UWIL, analyses performed by the University of Waterloo Environmental Isotope Laboratory; NSRL, analyses performed by the University of Rochester Nuclear Structures Research Laboratory; PRIME, analyses performed by Purdue University's PRIME Laboratory]

	Sample laboratory	Dissolved chloride concentration (mg/L)	( <sup>36</sup> Cl/Cl)×10 <sup>-15</sup>
Swipe before cleaning	UWIL	282±28	
	NSRL		263±21
Swipe after cleaning	UWIL	10±1	
	NSRL		5±10
	PRIME		5.8±4.0

The precipitate was filtered using a Millipore 250-mL filtering system with 0.45-µm cellulose nitrate filters. After filtration, the AgCl precipitate was washed several times with dilute ultrapure HNO<sub>3</sub>. A few drops of ultrapure AgNO<sub>3</sub> were added to an aliquot of the filtrate to test for any remaining, unprecipitated Cl. The AgCl was dissolved by the addition of 10 to 20 mL of 4 M ultrapure ammonium hydroxide (NH<sub>4</sub>OH) to the filter cup. Several rinses with 4 M NH<sub>4</sub>OH ensured that all of the Cl was transferred to the test tube.

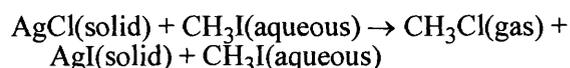
To remove sulfate from the AgCl precipitate, an ultrapure barium nitrate (Ba(NO<sub>3</sub>)<sub>2</sub>) solution was prepared by adding 100 mL of 1 M ultrapure HNO<sub>3</sub> to an excess of ultrapure barium carbonate (BaCO<sub>3</sub>) (approximately 25 g). A few drops of Ba(NO<sub>3</sub>)<sub>2</sub> solution then were added to the sample to remove sulfate according to the following reaction:



The sample was allowed to stand overnight to ensure complete precipitation of the barium sulfate (BaSO<sub>4</sub>). The sample was gravity filtered, and the precipitate was washed and discarded. The sample then was acidified to pH 1 by the addition of concentrated ultrapure HNO<sub>3</sub>. This resulted in the reprecipitation of AgCl. The AgCl precipitate was isolated by centrifugation. After three washing and recentrifugation steps, the final product was dried overnight in an oven at 90°C. Samples then were stored in amber glass vials to prevent photodecomposition of the AgCl.

The δ<sup>37</sup>Cl of a sample was determined by measurement of the <sup>37</sup>Cl/<sup>35</sup>Cl ratio of methyl chloride (CH<sub>3</sub>Cl) on a mass spectrometer

(Eggenkamp, 1994). The chloride ions in solution were precipitated by the addition of AgNO<sub>3</sub> at pH less than 2. The 6 to 10 mg of AgCl were transferred to a reaction vessel, evacuated, and an excess (30 µL) of methyl iodide (CH<sub>3</sub>I) was added. After 40-48 hours at 90°C, CH<sub>3</sub>Cl was formed.



The reaction vessel was attached to a preparation line where the CH<sub>3</sub>Cl/CH<sub>3</sub>I mixture was pushed with ultrapure helium through a gas chromatograph (Shimadzu-Porapak Q column). The methyl compounds were separated and the purified CH<sub>3</sub>Cl was placed in a vessel for mass spectrometric analysis on a VG SIRA 9 triple collector. The results were compared to commercial CH<sub>3</sub>Cl gas. No international standards for δ<sup>37</sup>Cl are available; therefore, all results were reported relative to SMOC which has been analyzed extensively by the UWIL and other laboratories. For the δ<sup>37</sup>Cl values listed in table 2, the associated uncertainties were calculated from duplicate and triplicate analyses as noted. Otherwise, an associated uncertainty of 0.2 permil was determined from all measurements made during 1993 and was assigned to those values determined from a single analysis.

### Quality Assurance

In addition to the measures described in the 'Analytical Methods' section, quality assurance and reproducibility of measurements for δ<sup>37</sup>Cl, dissolved Cl and <sup>36</sup>Cl concentrations were tested seven ways: (1) National Institute of Standards and Technology (NIST) standard reference materials were used to calibrate the accelerators for mass-spectrometric measurements at NSRL, PRIME, and Chalk River Laboratory (CRL); (2) two

prepared blank-water samples were measured for  $^{36}\text{Cl}/\text{Cl}$  at CRL; (3) five blind-replicate samples were analyzed for dissolved chloride at the NWQL and one blind-replicate sample was analyzed for  $^{36}\text{Cl}$  at CRL; (4) one laboratory blank was analyzed for  $^{36}\text{Cl}/\text{Cl}$  at the PRIME laboratory and a prepared spike sample was analyzed for Cl at UWIL; (5) SMOC was measured once for each 6 to 8 water samples and NIST standard 975 was measured periodically; (6) the SMOC used at the UWIL was analyzed at the University of Arizona's laboratory for comparison; and (7) replicate water samples were analyzed for  $^{36}\text{Cl}$  several months apart.

The NSRL, PRIME, and CRL facilities calibrate their respective AMS systems with prepared solutions of  $^{36}\text{Cl}$  traceable to NIST. Each AMS facility uses a solution prepared with  $^{36}\text{Cl}$  of known radioactivity with the addition of an appropriate amount of  $^{36}\text{Cl}$ -free chloride carrier. Control charts and documentation of the results of the calibrations are available for review at each facility.

Two AgCl targets were prepared using  $^{36}\text{Cl}$ -free potassium chloride supplied by the CRL using the precipitation method outlined in the 'Analytical Methods' section. One AgCl target was prepared using reagent-grade chemicals and a second target was prepared using ultrapure-grade chemicals. The  $^{36}\text{Cl}/\text{Cl}$  for the sample prepared with reagent-grade chemicals was  $18.9 \pm 6.7 \times 10^{-15}$ . The  $^{36}\text{Cl}/\text{Cl}$  for the sample prepared with ultrapure-grade chemicals was  $1.4 \pm 0.99 \times 10^{-15}$ . On the basis of these results, the decision was made to use ultrapure-grade chemicals for all AgCl target preparation for AMS.

Results of the blind-replicate analyses performed by NWQL for chloride concentrations are listed in table 4. All primary and blind-replicate analyses agree at the 95 percent confidence level using equation 2 (page 22) with the exception of the sample from USGS 14 collected October 1, 1993. However, the result of the blind-replicate analysis for the sample collected on this date was within 6.6 percent of the result of the primary-sample analysis. Therefore, it was concluded that the primary analysis was acceptable as being representative of the chloride concentration in water from USGS 14 collected on this date. One blind-replicate sample

was submitted to CRL for comparison to the primary sample submitted to PRIME lab for  $^{36}\text{Cl}$  analysis. The  $^{36}\text{Cl}/\text{Cl}$  for the primary sample was  $580 \pm 60 \times 10^{-15}$  and for the replicate the  $^{36}\text{Cl}/\text{Cl}$  was  $705 \pm 70 \times 10^{-15}$ . These two analyses were in statistical agreement at the 95 percent confidence level.

One prepared blank and one prepared spike sample were analyzed as part of the quality assurance for this study. A water sample was prepared at the PRIME lab with  $^{36}\text{Cl}$ -free chloride carrier and analyzed with the samples submitted from this study. The  $^{36}\text{Cl}/\text{Cl}$  in the prepared blank was  $12 \pm 2 \times 10^{-15}$  which was insignificant when compared to the results in table 2. This ratio was used, however, to blank correct the ratios presented in table 2. A spike sample with 100 mg/L chloride was prepared and submitted to UWIL for dissolved chloride analysis. The dissolved chloride concentration was  $118 \pm 12$  mg/L, which was in statistical agreement with the spike concentration.

As part of the quality assurance/quality control for this project, several water samples were measured for  $^{36}\text{Cl}/\text{Cl}$  ratios at both PRIME Laboratory and the NSRL. There was statistical agreement between the results reported from the two laboratories on blind-replicate samples and on duplicates of the same sample analyzed several months apart (Beasley and others, 1993, table 1).

## EVALUATION OF ARCHIVED WATER SAMPLES

To determine the quality and quantity of the archived samples, a complete inventory of the thousands of ground- and surface-water samples collected from 1966 through 1990 was conducted during February and March 1991. Samples were discarded that had questionable containers or did not have a complete historical record. The historical record for each sample included field notes taken during collection, laboratory notes compiled during analyses, chain-of-custody records maintained during processing (if available), and results of analyses requested and performed. The remaining samples were inventoried and a list is available in paper and digital form at the INEEL.

**Table 4.** Statistical comparison of chloride concentrations in primary- and blind-replicate water samples collected from selected wells, Idaho National Engineering and Environmental Laboratory, Idaho  
 [See figure 1 for location of wells. Analytical uncertainties expressed as one sample standard deviation estimated using equation 3 in text. All analyses performed by the U.S. Geological Survey National Water Quality Laboratory, Arvada, CO.]

Site identifier	Date sampled	Concentration and analytical uncertainty, in milligrams per liter		Test statistic, if A>B, analytical results are statistically different; see text for explanation		Results are statistically different
		Primary	Replicate	A	B	
USGS 14	10/01/93	18±1	21±1	3	2.8	yes
USGS 19	10/01/93	11±0.7	11±0.7	0	1.7	no
USGS 44	11/01/93	20±1	19±1	1	2.8	no
USGS 57	10/12/93	180±7	190±8	10	2.08	no
USGS 85	11/04/93	74±3	73±7	1	8.3	no

Approximately 200 of the water samples were selected for possible processing for  $^{36}\text{Cl}$  analyses. The analyses were based on location of sampling site, place in historical record, amount of water available, results of a  $^{36}\text{Cl}$  survey of ground water from the Snake River Plain aquifer from 1990–91 (Cecil and others, 1992; and Beasley and others, 1993), the dissolved chloride concentration, and sample/record integrity. Archived-water samples collected from six sites over a number of years were selected for comparison to the results of water samples collected in 1993 at the same sites (fig. 1). These samples were forwarded to the UWIL for determination of  $\delta^{37}\text{Cl}$ .

Eggenkamp (1994) lists 430  $\delta^{37}\text{Cl}$  values measured in water and rock samples by various researchers.  $\delta^{37}\text{Cl}$  values presented ranged from -4.9 to +6.0 permil, about 11 permil variation. In approximately 96 percent of the samples,  $\delta^{37}\text{Cl}$  ranged from -1.4 to +1.5 permil and 62 percent of the samples ranged from -0.4 to +0.5 permil. The average value for the 430 samples presented was -0.13 permil. The samples were collected from various geologic and hydrologic environments, from volcanic to carbonate rocks, and low-salinity to high-salinity ground water.

The  $\delta^{37}\text{Cl}$  data presented in this report for water samples collected from the eastern Snake River Plain aquifer ranged from -0.44 to +0.59 permil

with a mean of +0.14 permil (fig. 4 and table 2). The dissolved chloride concentrations used in figure 4 were the 1993 concentrations from table 2. This variation is much smaller than the variation for the 430 samples presented in the Eggenkamp review. The range of  $\delta^{37}\text{Cl}$  values in this study is similar to two-thirds of the values presented by Eggenkamp. A linear-regression analysis of the data presented in figure 4 produced a  $R^2$  (fraction of variance explained by the regression) value of 0.07 suggesting no apparent correlation between dissolved Cl concentrations and  $\delta^{37}\text{Cl}$ .

In addition to determining the degree of fractionation of chlorine isotopes in the archived-water samples, dissolved Cl concentrations were redetermined in 1993 and compared to the Cl concentration at the time of sample collection. To determine if significant Cl had been lost from a water sample during storage, statistical comparisons of Cl concentrations in samples collected from each site were made. Results from the 1993 analyses were compared to the results at the time of sample collection.

Water samples collected from well USGS 19 were selected as representative of ambient  $\delta^{37}\text{Cl}$  of the eastern Snake River Plain aquifer. Ambient values for this study are those values in water not affected by site disposal practices. However, these ambient values may have been affected by nuclear

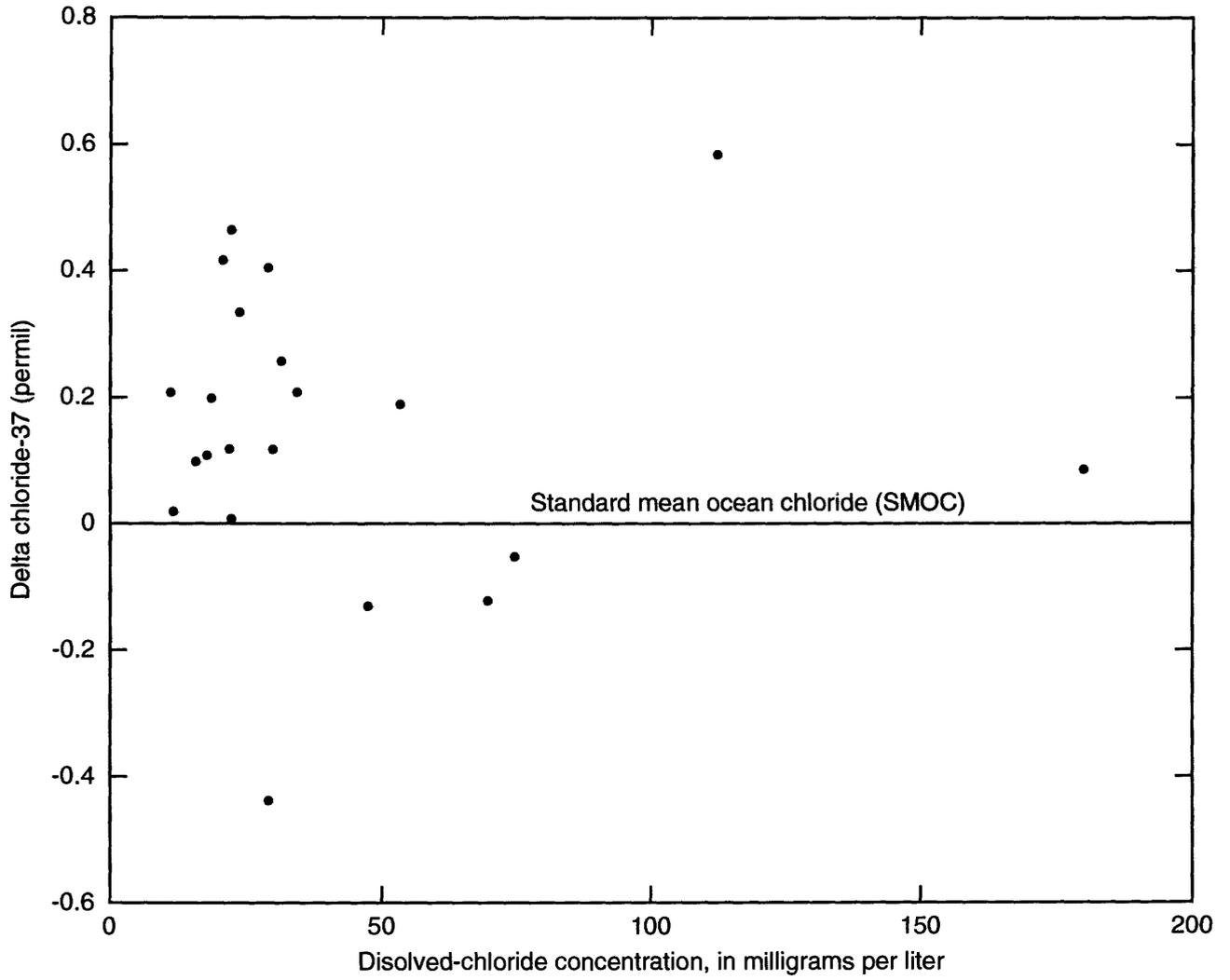


Figure 4. Dissolved-chloride concentration and delta chloride-37.

weapons testing and/or irrigation practices. The  $^{36}\text{Cl}$  concentrations listed in table 2 for water collected from USGS 19,  $1.1\pm 0.1$  to  $2.9\pm 0.3\times 10^8$  atoms/L, indicate there has been some influence from anthropogenic sources. Additionally, the dissolved Cl concentration for water collected from USGS 19 sampled in 1969,  $29.0\pm 2.9$  mg/L (table 2), indicates an anthropogenic influence on the water because background Cl concentrations are 10 mg/L or less for the eastern Snake River Plain aquifer (Robertson and others, 1974). This additional Cl may be due to surface flood-irrigation in practice since the mid 1930's in the Little Lost River drainage upgradient from USGS 19 (fig. 1). The  $\delta^{37}\text{Cl}$  values in water collected from USGS 19 ranged from  $0.02\pm 0.2$  to  $0.12\pm 0.2$  permil, not statistically different from SMOC, and may represent a true  $\delta^{37}\text{Cl}$  for water entering the Snake River Plain aquifer from the Little Lost River drainage. The  $\delta^{37}\text{Cl}$  for water collected on April 3, 1970, from the Little Lost River also had a  $\delta^{37}\text{Cl}$  value statistically the same as SMOC,  $+0.27\pm 0.23$  permil (table 2). The site where the Little Lost River sample was collected is about 18 km upgradient from USGS 19 (fig. 1).

None of the  $\delta^{37}\text{Cl}$  results for any of the wells listed in table 2 varied by more than 0.91 permil. This variation was in contrast to that presented by Eggenkamp (1994) for a greater variety of geologic media; the variation in that review was nearly 11 permil or an order of magnitude greater than the variation in water samples collected from the INEEL and vicinity. However, the  $\delta^{37}\text{Cl}$  data presented here are consistent with two-thirds of the values presented by Eggenkamp. The largest variance was for water collected from well USGS 14, the most distant well downgradient from the waste-chloride source, at the ICPP (fig. 1). Average chloride disposal to the Snake River Plain aquifer system has increased from 1971–93 (fig. 5). Concentrations of  $^{36}\text{Cl}$  significantly greater than background concentrations were first noticed in ground water at USGS 14 about 1984 (fig. 6 and table 2). In 1984, the  $\delta^{37}\text{Cl}$  in water from this well showed a shift from positive values to a negative value suggesting waste-stream influences from ICPP. The most negative  $\delta^{37}\text{Cl}$  value ( $-0.13\pm 0.1$ ) and the largest  $^{36}\text{Cl}/\text{Cl}$  ( $21,000\pm 580\times 10^{-13}$ ) in water samples collected from well USGS 57, the

well located nearest to the discharge point at ICPP, was in 1969. The next most negative value ( $-0.12\pm 0.01$ ) and the next largest  $^{36}\text{Cl}/\text{Cl}$  ( $19,300\pm 640\times 10^{-13}$ ) occurred in 1988 (fig. 7 and table 2). The most positive  $\delta^{37}\text{Cl}$  values in water from USGS 14 and 57 were in thief samples, which also had the smallest  $^{36}\text{Cl}$  concentrations; 1982 for USGS 14, and 1983 for USGS 57. This suggests an inverse correlation between  $\delta^{37}\text{Cl}$  and  $^{36}\text{Cl}$  concentrations in the waste effluent from ICPP. The  $^{36}\text{Cl}$  concentrations for USGS 57 (fig. 7) are nearly four orders of magnitude greater than the concentrations shown for USGS 14 (fig. 6) due to the closer proximity of USGS 57 to the disposal well and ponds at ICPP. The additional  $^{36}\text{Cl}$  data for wells USGS 57 and USGS 14 shown on figures 6 and 7 that are not listed in table 2 are available for inspection at the USGS Project Office at the INEEL.

Water collected from wells USGS 19, 20, 44, and 57 showed this same inverse correlation in samples collected by the thief method; the larger  $^{36}\text{Cl}$  concentrations are associated with the smaller  $\delta^{37}\text{Cl}$ . With the exception of USGS 85, all pumped samples had a positive  $\delta^{37}\text{Cl}$  and range from  $+0.02$  to  $+0.42$  permil; the pumped sample from USGS 85 was  $-0.05$  permil.

The most negative  $\delta^{37}\text{Cl}$  values occurred on the same dates as the largest  $^{36}\text{Cl}$  concentrations in water collected from wells USGS 57 and 14, also suggesting an inverse correlation between  $\delta^{37}\text{Cl}$  and  $^{36}\text{Cl}$  concentrations. Wells 19, 20, and 44 had no negative  $\delta^{37}\text{Cl}$  values in either thief or pumped samples. It should also be noted that water collected May 8, 1969 from well USGS 57 had the largest  $^{36}\text{Cl}/\text{Cl}$ ,  $21,000\pm 580\times 10^{-13}$ , and also had the smallest dissolved chloride concentration,  $46.9\pm 4.7$  mg/L (table 2). This suggests that measured  $^{36}\text{Cl}$  concentrations in ground water from the eastern Snake River Plain aquifer are a more sensitive indicator of contaminant transport at the ICPP than tritium or iodine-129.

The data presented here further suggest that processes fractionating stable chlorine isotopes or that are adding chloride with a ratio different from SMOC in the eastern Snake River Plain aquifer are from the facilities at the INEEL and that from the data presented here, no natural processes are

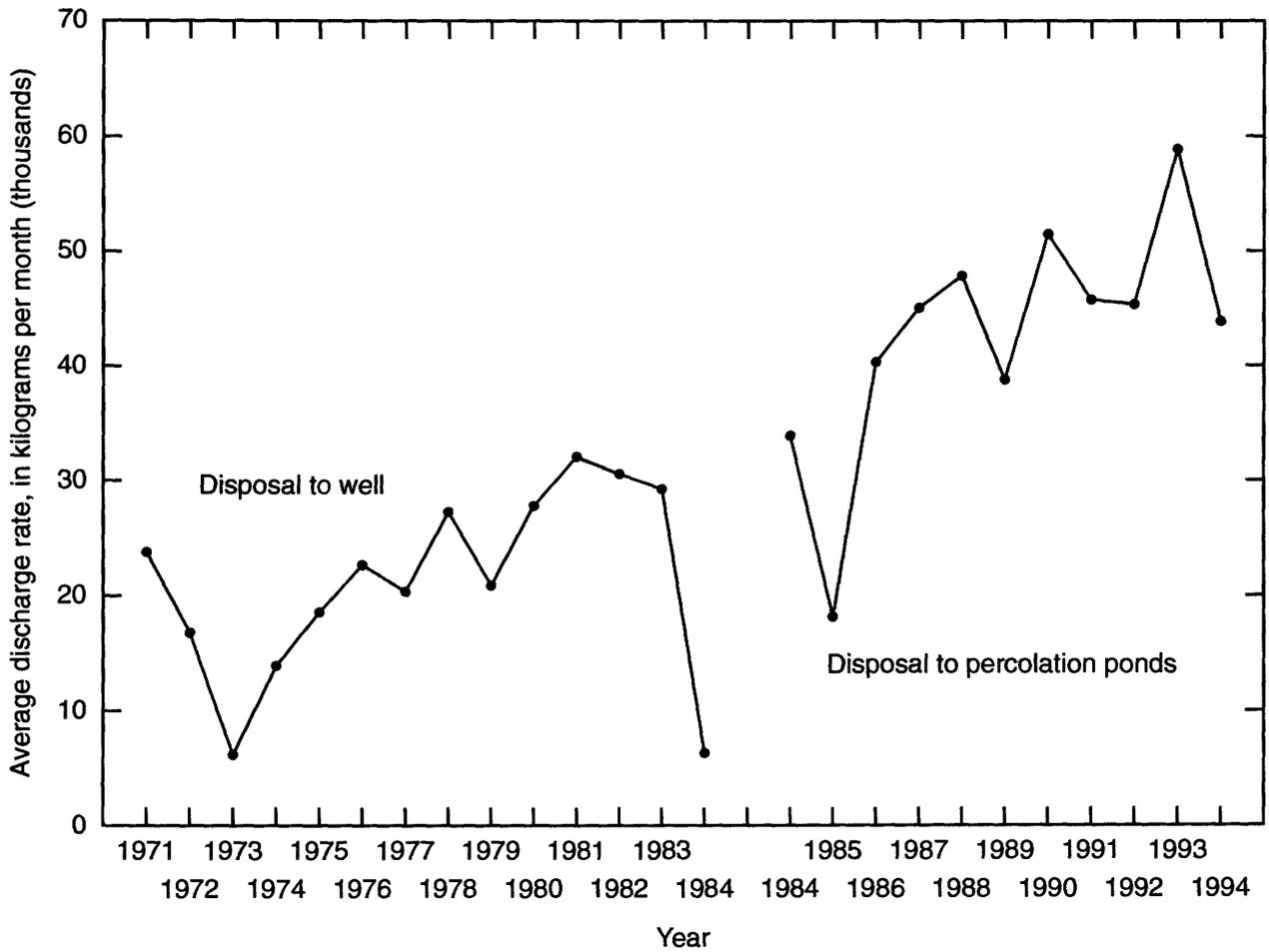


Figure 5. Average annual chloride discharge rate at the Idaho Chemical Processing Plant, Idaho National Engineering and Environmental Laboratory, Idaho.

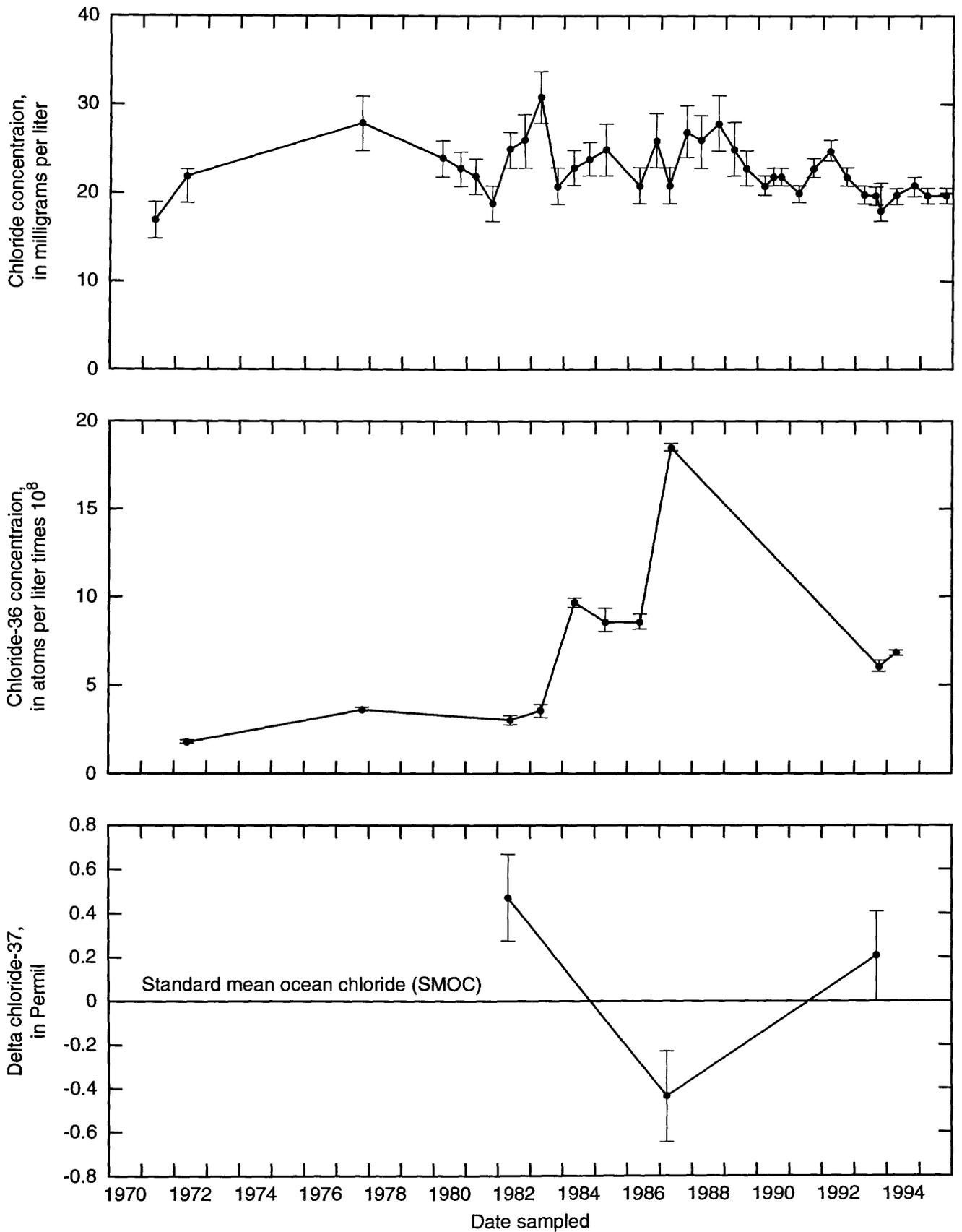


Figure 6. Concentrations of dissolved chloride, chloride-36, and delta chloride-37 in relation to time, in ground water from well USGS 14, Idaho National Engineering and Environmental Laboratory, Idaho.

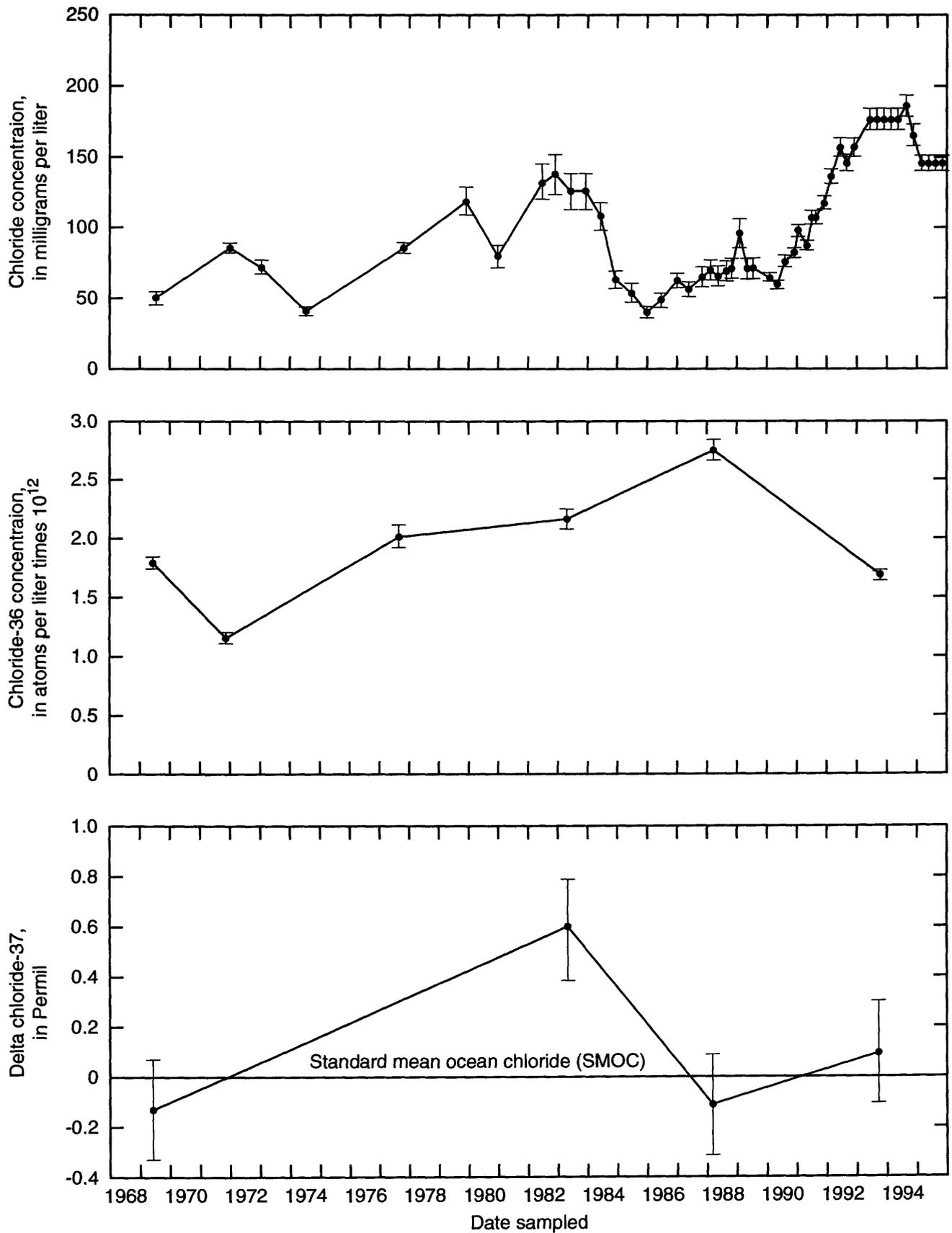


Figure 7. Concentrations of dissolved chloride, chloride-36, and delta chloride-37 in relation to time, in ground water from well USGS 57, Idaho National Engineering and Environmental Laboratory, Idaho.

quantifiable for chlorine isotope fractionation. These data further suggest that the radiochemical reprocessing of spent nuclear fuel at the ICPP may deplete the chloride released to the environment in terms of  $^{37}\text{Cl}/^{35}\text{Cl}$  as compared to SMOC. Evidence for this possibility comes from the inverse correlation of  $\delta^{37}\text{Cl}$  and  $^{36}\text{Cl}$  concentrations found in this evaluation and from the fact that in advective mixing of two sources of different concentrations, the larger concentration source (chloride from waste disposal at the ICPP) dominates the isotopic signature of the mixture. To confirm this possibility,  $\delta^{37}\text{Cl}$  measurements need to be performed on water from the effluent stream at the ICPP.

Comparison of chloride concentrations from the different sets of analyses was made using a modification of the t-test for unequal variances (Helsel and Hirsch, 1992, p. 126):

$$t = \frac{\bar{X} - \bar{Y}}{\sqrt{\frac{S_x^2}{n} + \frac{S_y^2}{m}}} \quad (1)$$

where:

$\bar{X}$  is the mean of data in the first group,

$\bar{Y}$  is the mean of data in the second group,

$S_x^2$  is the sample variance of the first group,

$S_y^2$  is the sample variance of the second group,

$n$  is the number of samples in the first group,

$m$  is the number of samples in the second group, and

$t$  is the test statistic.

The t-test can be used to determine if the means of two different sets of analyses are different. An assumption was made that the true variances for each set of chloride analyses presented in this report, performed by different methods from different laboratories, were in fact unequal. In this report, a modification to equation 1 was used. The following equation was used for the comparison where  $n$  and  $m$  from equation 1 are equal to one:

$$|X - Y| > 1.96((S_x^2) + (S_y^2))^{1/2} \quad (2)$$

where:

$X$  is the analytical result at the time of sample collection,

$Y$  is the analytical result, for the same sample as  $X$ , analyzed in 1993,

$S_x^2$  is the sample variance of  $X$ ,

$S_y^2$  is the sample variance of  $Y$ , and

1.96 is the test statistic ( $t$  in equation 1) for the 95 percent confidence limit (Taylor, 1987, table C.2, p. 266).

In equation 2, if the absolute value of  $X - Y$  exceeded the calculated value on the right-hand side of the equation, the two analytical results were considered to be statistically different. For this study, the statistical test for precision of results from the different methods was based on the sample standard deviations for reported concentrations from each laboratory. If the data were normally distributed and the sample standard deviations reported by the laboratories represented the true standard deviation, then the analytical results were considered to be statistically equal at the 95-percent confidence limit if  $|X - Y|$  was less than or equal to the right-hand side of equation 2.

Concentrations of dissolved Cl in the archived-water samples at the time of collection ranged from  $12 \pm 1$  to  $127 \pm 13$  mg/L (table 2). The results of Cl analyses on these same archived-water samples in 1993 ranged from  $10.6 \pm 1.1$  to  $112 \pm 11.2$  mg/L. The concentrations reported by RESL for the archived samples and by UWIL for the analyses in 1993 have associated uncertainties reported as one sample standard deviation estimated as 10 percent of the reported concentration. These sample standard deviations estimated as  $\pm 10$  percent for the chloride results reported by the RESL and UWIL were substituted into equation 2 for  $S_x$  and  $S_y$ . Therefore, this statistical evaluation must be considered as only a guide in testing for non-equivalence. These estimated standard deviations may not represent the true standard deviation of the reported concentrations.

The results of chloride analyses performed by the NWQL and presented in table 2 also were not reported with a sample standard deviation, therefore, estimations of sample standard deviations were calculated. The USGS Branch of Quality

Assurance conducts a Blind Sample Program (BSP) in which reference samples disguised as environmental samples are submitted to the NWQL for analyses (Maloney and others, 1993). These BSP data are stored in the USGS data base (QADATA) and are accessible through the USGS computer system (Lucey, 1990). The statistical analyses generated through the QADATA program include equations generated by using linear-least-squares regression of a most probable value for a given analyte from the USGS's standard reference water-sample program during the previous 7 years against a corresponding sample standard deviation for that analyte. These linear-regression equations facilitate the calculation of a most probable deviation (MPD) at most concentrations for most analytes. The following equation from Maloney and others (1993) was used to estimate the sample standard deviations, or MPD, in table 2 and 4 for chloride concentrations reported by the NWQL:

$$y = 0.039x + 0.3 \quad (3)$$

where:

$x$  is the reported chloride concentration, and  
 $y$  is the calculated sample standard deviation.

Comparison of Cl concentrations at the time of sample collection to the concentration determined in 1993 on the same samples, indicated that the concentrations were statistically the same at the 95 percent confidence level in all cases except for samples collected April 8, 1987, from USGS 14 and April 8, 1983 from USGS 19 (table 5). For the Cl concentration in water from USGS 14, the smaller concentration was the value at the time of sample collection. Therefore, the Cl concentration for the sample collected on April 8, 1987 at USGS 14 may be a conservative estimate of the true concentration. At USGS 19, the larger of the two concentrations listed in table 5 was the concentration at the time of sample collection on April 8, 1983;  $21 \pm 1$  mg/L. This suggests that the estimate of the  $^{36}\text{Cl}$  concentration for water collected on this date may be as much as 29 percent too large.

## SUMMARY

The U.S. Department of Energy (DOE) requires information about the mobility and/or retardation

of radiochemical and chemical wastes released to the environment at the Idaho National Engineering and Environmental Laboratory (INEEL). In 1949, the DOE (then called the Atomic Energy Commission) requested the U.S. Geological Survey (USGS) to describe the geology and water resources of the eastern Snake River Plain. Since the completion of that initial site characterization, the USGS has maintained a network of monitoring wells to determine hydrologic trends and to describe the fate of contaminants contained in wastewater released to the environment. Since 1966, the USGS routinely has archived at least one suite of quarterly water samples collected at the INEEL. This report presents the results of an evaluation of the archived ground- and surface-water samples at the INEEL for the period 1966–93.

Stable chlorine isotopic ratios, chlorine-37/chlorine-35 ( $^{37}\text{Cl}/^{35}\text{Cl}$ ), were determined on 21 ground-water samples collected from 6 USGS observation wells for 1966–93 and from one surface-water site for 1970. The  $^{37}\text{Cl}/^{35}\text{Cl}$  ratio from the archived samples was measured at the Environmental Isotope Laboratory at the University of Waterloo (UWIL) and was compared to the  $^{37}\text{Cl}/^{35}\text{Cl}$  of Standard Mean Ocean Chloride (SMOC). The resultant delta  $^{37}\text{Cl}$  ( $\delta^{37}\text{Cl}$ ) ranged from -0.44 to +0.59 permil and had a mean of +0.14 permil. The largest variation in  $\delta^{37}\text{Cl}$  for water from any individual well was 0.91 permil. A review of available  $\delta^{37}\text{Cl}$  data collected worldwide from a large variety of geologic and hydrogeologic environments, showed a range of -4.9 to +6.0 permil which is nearly 11 permil and is an order of magnitude greater than the range of  $\delta^{37}\text{Cl}$  for water collected from the INEEL and vicinity. The range of  $\delta^{37}\text{Cl}$  values in ground water collected from the INEEL is indicative of little or no measurable fractionation. The range of  $\delta^{37}\text{Cl}$  values in water collected from well USGS 19 represented ambient values and were not statistically different than SMOC from 1969–93. Therefore, negative  $\delta^{37}\text{Cl}$  was attributable to wastewater disposal and not to any processes operational during sample storage in the archive library or along the flowpath in the Snake River Plain aquifer.

**Table 5.** Statistical comparison of chloride concentrations at time of sample collection and chloride concentration in 1993 for archived ground-water samples

[See figure 1 for location of wells. Analytical uncertainties expressed as one sample standard deviation estimated as 10 percent of the analytical result; RESL, Radiological and Environmental Sciences Laboratory; UWIL, University of Waterloo Environmental Isotope Laboratory; nr indicates that analysis and statistical test were not performed]

Site identifier	Date sampled	Concentration and analytical uncertainty, in milligrams per liter		Test statistic, if A>B, analytical results are statistically different; see text for explanation		Results are statistically different
		RESL (time of collection)	UWIL (1993)	A	B	
USGS 14	04/14/82	25±2	21.4±2.1	3.6	5.7	no
	04/08/87	21±2	28.4±2.8	7.4	6.7	yes
USGS 19	10/20/69	nr	29.0±2.9	nr	nr	nr
	04/08/83	21±1	14.9±1.5	6.1	4.9	yes
USGS 20	04/28/69	30±3	30.7±3.1	.7	6.1	no
	04/12/83	24±2	21.6±2.2	2.4	5.8	no
	04/04/88	24±2	28.2±2.8	4.2	6.7	no
USGS 44	05/08/69	12±1	10.6±1.1	1.4	2.9	no
	04/12/83	59±6	52.8±5.2	6.2	15.6	no
	04/09/88	15±2	17.0±1.7	2.0	5.1	no
USGS 57	05/08/69	50±5	46.9±4.7	3.1	13.4	no
	04/12/83	127±13	112±11.2	15	33.6	no
	03/31/88	67±7	69.2±6.9	2.2	19.3	no
USGS 85	04/25/69	24±2	21.3±2.1	2.7	5.7	no
	04/13/83	37±4	33.8±3.4	3.2	10.3	no

Radioactive chlorine ( $^{36}\text{Cl}$ ) concentrations also were measured in the archive-water samples selected for this evaluation. The historical  $^{36}\text{Cl}$  concentrations ranged from  $1.1 \pm 0.1 \times 10^8$  atoms/liter to  $28,000 \pm 910 \times 10^8$  atoms/liter. Based on the evaluation of the archived water samples in terms of  $\delta^{37}\text{Cl}$ , it was concluded that the  $^{36}\text{Cl}$  concentrations measured in 1993 were representative of the concentrations at the time of sample collection.

Quality assurance and reproducibility of measurements for  $\delta^{37}\text{Cl}$ , dissolved Cl and  $^{36}\text{Cl}$  concentrations for this study were tested in seven ways: (1) National Institute of Standards and Technology (NIST) standard reference materials were used to calibrate the accelerators for mass spectrometric measurements at the University of Rochester's Nuclear Structure Research Laboratory, PRIME Laboratory, at Purdue University, and Chalk River Laboratories, Ontario, Canada (CRL); (2) two prepared blank-water

samples were measured for  $^{36}\text{Cl}/\text{Cl}$  at CRL; (3) five blind-replicate samples were analyzed for dissolved chloride at the USGS's National Water Quality Laboratory and one blind-replicate sample was analyzed for  $^{36}\text{Cl}$  at CRL; (4) one laboratory blank was analyzed for  $^{36}\text{Cl}/\text{Cl}$  at PRIME Laboratory and a prepared spike sample was analyzed for Cl at UWIL; (5) SMOC was measured once for each 6 to 8 water samples and NIST standard 975 was measured periodically; (6) the SMOC used at the UWIL was analyzed at the University of Arizona's laboratory for comparison; and (7) replicate water samples were analyzed for  $^{36}\text{Cl}$  several months apart. All quality-control samples met the criteria of reproducibility selected for this study.

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