

Prepared in cooperation with the U.S. Environmental Protection Agency

# Evaluation of Ground-Water and Boron Sources by Use of Boron Stable-Isotope Ratios, Tritium, and Selected Water-Chemistry Constituents near Beverly Shores, Northwestern Indiana, 2004



Scientific Investigations Report 2007–5166

**Cover:** Photographs showing examples of potential sources of boron in shallow ground water that were considered by this investigation: A natural source of boron in artesian flow from a well developed in the basal sand aquifer near Beverly Shores, Indiana; coal-combustion product at land surface near the Town of Pines, Indiana; and a suspected seep of domestic-wastewater-affected ground water at Beverly Shores, Indiana. (Photographs by Lee R. Watson, March 28, 2005.)

# **Evaluation of Ground-Water and Boron Sources by Use of Boron Stable-Isotope Ratios, Tritium, and Selected Water-Chemistry Constituents near Beverly Shores, Northwestern Indiana, 2004**

By Paul M. Buszka, John Fitzpatrick, Lee R. Watson, and Robert T. Kay

Prepared in cooperation with the U.S. Environmental Protection Agency

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## Conversion Factors, Water-Quality Units, and Abbreviations

### Inch/Pound to Metric (SI) units

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
inch (in.)	$2.54 \times 10^{-4}$	micrometer ( $\mu\text{m}$ )
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
acre	0.4047	hectare (ha)
square mile ( $\text{mi}^2$ )	259.0	hectare (ha)
Volume		
gallon (gal)	3.785	liter (L)
gallon (gal)	$3.785 \times 10^3$	milliliter (mL)
gallon (gal)	$3.785 \times 10^6$	microliter ( $\mu\text{L}$ )
Flow rate		
gallon per minute (gal/min)	0.06309	liter per second (L/s)
Mass		
ounce, avoirdupois (oz)	28.35	gram (g)
pound, avoirdupois (lb)	0.4536	kilogram (kg)
Pressure		
atmosphere, standard (atm)	101.3	kilopascal (kPa)
bar	100	kilopascal (kPa)

Temperature in degrees Fahrenheit ( $^{\circ}\text{F}$ ) may be converted to degrees Celsius ( $^{\circ}\text{C}$ ) as follows:

$$^{\circ}\text{C}=(^{\circ}\text{F}-32)/1.8$$



## Conversion Factors, Water-Quality Units, and Abbreviations—Continued

### Metric (SI) to Inch/Pound units

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	$3.987 \times 10^{-2}$	inch (in.)
micrometer ( $\mu\text{m}$ )	$3.987 \times 10^{-5}$	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
Area		
hectare (ha)	2.471	acre
hectare (ha)	0.003861	square mile ( $\text{mi}^2$ )
Volume		
liter (L)	0.2642	gallon (gal)
milliliter (mL)	$2.642 \times 10^{-4}$	gallon (gal)
microliter ( $\mu\text{L}$ )	$2.642 \times 10^{-7}$	gallon (gal)
Flow rate		
liter per second (L/s)	951	gallon per minute (gal/min)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
Pressure		
pascal (Pa)	$9.869 \times 10^{-6}$	atmosphere, standard (atm)
pascal (Pa)	$1 \times 10^{-5}$	bar

Temperature in degrees Celsius ( $^{\circ}\text{C}$ ) may be converted to degrees Fahrenheit ( $^{\circ}\text{F}$ ) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83). Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29).

Altitude, as used in this report, refers to distance above the vertical datum.

## Conversion Factors, Water-Quality Units, and Abbreviations—Continued

Electrical units used in this report are given in metric units. Units of electrical current are reported as amperes. An ampere is a base unit of electric current, or amount of electric charge per second. Units of potential difference in this report are reported in volts and kilovolts. A volt is the difference in potential across a conductor under one watt of power and a current of one ampere. One kilovolt equals one thousand volts. Units of resistance in this report are reported as ohms. An ohm is the electrical resistance of a conductor that causes a one volt drop in potential across a conductor under a current of one ampere.

Abbreviated water-quality units used in this report: Chemical concentrations and water temperature are given in metric units. Concentrations of chemical constituents in water are given in units of milligram per liter (mg/L) or microgram per liter ( $\mu\text{g/L}$ ). A milligram per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligram) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. For concentrations less than 7,000 mg/L, the numerical value for milligrams per liter is the same as for concentrations in part per million.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ( $\mu\text{S/cm}$  at 25°C).

An atomic mass unit (amu) is used to represent atomic and molecular masses. An amu is defined as one-twelfth of the mass of an atom of the carbon isotope carbon-12, at rest and in its ground state.

$1 \text{ amu} = 1/N_A \text{ g}$  (where  $N_A$  is Avogadro's number or about  $6.022 \times 10^{23}$  and g is 1 gram of the element)

Concentrations in some computations are reported in units of micromole per liter. A mole of a substance is its atomic or formula weight in grams. A concentration of a substance reported as a microgram per liter can be converted to a concentration in micromole per liter by dividing by the atomic or formula weight of the substance, in grams.

One tritium unit (TU) is equivalent to a concentration of 3.2 picocuries per liter.

$\delta$  (delta), as used in this report, refers to the stable-isotope ratio  $\delta x = \{ [R_x - R_{\text{std}}] / R_{\text{std}} \} * 1000$ , where  $R_x$  and  $R_{\text{std}}$  are the  $^{11}\text{B}/^{10}\text{B}$  and  $^{18}\text{O}/^{16}\text{O}$  values of the sample and reference standard. The value of  $\delta$  generally is expressed in parts per thousand (‰, or per mil). Per mil, as used in this report, is equivalent to parts per thousand.

The ratio of the isotopes strontium-87 to strontium-86 is reported as a molar ratio. The molar ratio of strontium-87 to strontium-86 is computed by dividing the concentration of strontium-87 in moles per liter, by the concentration of strontium-86, in moles per liter. A molar ratio is dimensionless.

## Conversion Factors, Water-Quality Units, and Abbreviations—Continued

### Abbreviations and Acronyms used in this report:

<b>A</b>	Ampere
<b>amu</b>	Atomic mass unit
<b>B</b>	Boron
<b><sup>10</sup>B</b>	Boron-10 stable isotope
<b><sup>11</sup>B</b>	Boron-11 stable isotope
<b>CCP</b>	Coal-combustion product (fly ash and bottom ash)
<b>DI</b>	Deionized
<b>N</b>	Nitrogen
<b>NIST</b>	National Institute of Standards and Technology
<b>NPS</b>	National Park Service
<b>NTIMS</b>	Negative-ion mode thermal ionization mass spectrometry
<b>NTU</b>	Nephelometric turbidity units
<b>O</b>	Oxygen
<b>PTIMS</b>	Positive-ion mode thermal ionization mass spectrometry
<b>RAL</b>	Removal action level
<b>SA</b>	Surficial aquifer
<b>TU</b>	Tritium unit
<b>USEPA</b>	U.S. Environmental Protection Agency
<b>USGS</b>	U.S. Geological Survey



# Evaluation of Ground-Water and Boron Sources by Use of Boron Stable-Isotope Ratios, Tritium, and Selected Water-Chemistry Constituents near Beverly Shores, Northwestern Indiana, 2004

By Paul M. Buszka, John Fitzpatrick, Lee R. Watson, and Robert T. Kay

## Abstract

Concentrations of boron greater than the U.S. Environmental Protection Agency (USEPA) 900  $\mu\text{g/L}$  removal action level (RAL) standard were detected in water sampled by the USEPA in 2004 from three domestic wells near Beverly Shores, Indiana. The RAL regulates only human-affected concentrations of a constituent. A lack of well logs and screened depth information precluded identification of whether water from sampled wells, and their boron sources, were from human-affected or natural sources in the surficial aquifer, or associated with a previously defined natural, confined aquifer source of boron from the subsoil or basal sand aquifers. A geochemically-based classification of the source of boron in ground water could potentially determine the similarity of boron to known sources or mixtures between known sources, or classify whether the relative age of the ground water predated the potential sources of contamination. The U.S. Geological Survey (USGS), in cooperation with the USEPA, investigated the use of a geochemical method that applied boron stable isotopes, and concentrations of boron, tritium, and other constituents to distinguish between natural and human-affected sources of boron in ground water and thereby determine if the RAL was applicable to the situation.

Boron stable-isotope ratios and concentrations of boron in 17 ground-water samples and tritium concentrations in 9 ground-water samples collected in 2004 were used to identify geochemical differences between potential sources of boron in ground water near Beverly Shores, Indiana. Boron and  $\delta^{11}\text{B}$  analyses for this investigation were made on unacidified samples to assure consistency of the result with unacidified analyses of  $\delta^{11}\text{B}$  values from other investigations. Potential sources of boron included surficial-aquifer water affected by coal-combustion products (CCP) or domestic-wastewater, upward discharge of ground water from confined aquifers, and unaffected water from the surficial aquifer that was distant from human-affected boron sources.

Boron concentrations in potential ground-water sources of boron were largest (15,700 to 24,400  $\mu\text{g/L}$ ) in samples of CCP-affected surficial aquifer water from four wells at a CCP landfill and smallest (27 to 63  $\mu\text{g/L}$ ) in three wells in the surficial aquifer that were distant from human-affected boron sources. Boron concentrations in water from the basal sand aquifer ranged from 656  $\mu\text{g/L}$  to 1,800  $\mu\text{g/L}$ . Boron concentrations in water from three domestic-wastewater-affected surficial aquifer wells ranged from 84 to 387  $\mu\text{g/L}$ . Among the representative ground-water samples, boron concentrations from all four samples of CCP-affected surficial aquifer water and four of five samples of water from the basal sand aquifer had concentrations greater than the RAL. A comparison of boron concentrations in acid-preserved and unacidified samples indicated that boron concentrations reported for this investigation may be from about 11 to 16 percent less than would be reported in a standard analysis of an acidified sample.

The stable isotope boron-11 was most enriched in comparison to boron-10 in ground water from a confined aquifer, the basal sand aquifer ( $\delta^{11}\text{B}$ , 24.6 to 34.0 per mil, five samples); it was most depleted in CCP-affected water from the surficial aquifer ( $\delta^{11}\text{B}$ , 0.1 to 6.6 per mil, four samples). Domestic-wastewater-affected water from the surficial aquifer ( $\delta^{11}\text{B}$ , 8.7 to 11.7 per mil, four samples) was enriched in boron-11, in comparison to individual samples of a borax detergent additive and a detergent with perborate bleach; it was intermediate in composition between basal sand aquifer water and CCP-affected water from the surficial aquifer. The similarity between a ground-water sample from the surficial aquifer and a hypothetical mixture of unaffected surficial aquifer and basal sand aquifer waters indicates the potential for long-term upward discharge of ground water into the surficial aquifer from one or more confined aquifers. Estimated  $\delta^{11}\text{B}$  values for acidified samples were depleted by 1.9 to 2.8 per mil in comparison to unacidified samples from the four wells sampled; those differences were small in comparison to the differences between  $\delta^{11}\text{B}$  values of representative sources of boron in ground water.

## 2 Evaluation of Ground-Water and Boron Sources near Beverly Shores, Northwestern Indiana, 2004

Tritium concentrations ranged from 7.0 to 10.3 tritium units in six samples from the surficial aquifer and were less than 0.8 tritium units in three samples from the basal sand aquifer. Water from wells in the surficial aquifer represents predominantly modern, post-1972 recharge and sources of boron and other constituents. Water from the basal sand aquifer is associated with pre-1952 recharge from sources not affected by local boron inputs.

Ground water from six wells (five domestic wells and one public-supply well) where the ground-water source was unknown had boron concentrations, boron isotope ratios, and tritium concentrations similar to water from the basal sand aquifer. Boron concentrations greater than the RAL were found in water from four of these six wells. The boron isotope and tritium data from these four wells indicate a natural source of boron in ground water; therefore, the RAL does not apply to boron concentrations in water from these wells. Water samples from two domestic wells where the ground-water source was unknown had boron concentrations less than the RAL and boron isotope ratios and tritium concentrations that were similar to domestic-wastewater-affected water from the surficial aquifer. The boron isotope ratio for a sample from one domestic well was similar to that of CCP-affected water from the surficial aquifer and detergent compositions; the boron concentration of that sample was less than the RAL. The classifications of differences among representative sources of boron in ground water and water samples from wells where the ground-water source was unknown generally agreed with distinctions based on strontium-87/strontium-86 ratios and concentrations of strontium, chloride, nitrate, and ammonia. This application of boron concentrations, boron isotope ratios, and tritium concentrations to classify differences in relation to potential sources of boron in ground water was able to distinguish between boron from natural sources and from human-affected sources that are subject to regulation.

## Introduction

In March 2004, sampling and analysis of ground water by the U.S. Environmental Protection Agency (USEPA) identified boron concentrations greater than 900  $\mu\text{g/L}$  in water from three domestic wells and from one well at a National Park Service facility near Beverly Shores in Porter County, northwestern Indiana (fig. 1) (Kenneth Theisen, U.S. Environmental Protection Agency, written commun., 2006). A separate 2004 USEPA sampling of water from a well at a local elementary school about 0.75 mi west of the nearby Town of Pines, Indiana identified boron at a concentration of 424  $\mu\text{g/L}$  and molybdenum at a concentration of 10.8  $\mu\text{g/L}$  (Kenneth Theisen, U.S. Environmental Protection Agency, written commun., 2007). Concentrations established as removal action levels (RALs) by the U.S. Environmental Protection Agency are 900  $\mu\text{g/L}$  for boron and 10  $\mu\text{g/L}$  for molybdenum (U.S. Environmental Protection Agency, 1998). RALs are used to

determine whether to provide alternate drinking-water supplies under Superfund removal authority when the source of the boron is human affected (U.S. Environmental Protection Agency, 1998).

The 2004 USEPA sampling and analytical results led to an emergency provision of bottled drinking water to Beverly Shores residents whose wells produced water with boron or molybdenum concentrations higher than a RAL. The sources of boron and molybdenum in ground water, however, were unknown. A lack of well logs and well-screen depth information precluded identification of whether water from many sampled wells, and their boron sources, were from the surficial aquifer, or associated with deeper, confined aquifers. A previous study found that water from two confined, glacial aquifers, the subfill aquifer and basal sand aquifer, had naturally higher concentrations of boron than the surficial aquifer; the higher concentrations probably related to discharge from the regional flow system (Shedlock and others, 1994). Methods were needed to distinguish the contribution of natural sources or human-affected sources of contamination to determine if the RAL was applicable to the situation.

The USEPA has interpreted concentrations of boron and molybdenum higher than the RAL in ground water and surface water near Pines to be from disposal of coal-combustion products (CCP) and leaching from the CCP into ground water (U.S. Environmental Protection Agency, 2006a). CCP (fly ash and bottom ash) from local electric-generating plants were used as a base for roads and driveways and as fill in topographic depressions in the Pines area for many years, or was disposed of from the 1960s until 2001 at the Yard 520 landfill (fig. 2) (U.S. Environmental Protection Agency, 2007; ENSR Corporation, 2005). Because boron has fewer precipitation and sorption limits on its transport in ground water (Bassett and others, 1995) relative to molybdenum (Hem, 1982; Fox and Doner, 2003), boron is likely a more conservative indicator of potential CCP sources in local ground water. In April 2004, the U.S. Geological Survey (USGS), in cooperation with the USEPA, began an investigation of whether boron concentrations in ground water near Beverly Shores and west of the nearby Town of Pines (fig. 1) were from natural or human-affected sources.

## Background Information

Boron in ground water may have several possible human-affected sources, including CCP, wastewater effluent, and laundry detergent; possible natural sources include leaching of geologic materials and mixing of ground water (Davidson and Bassett, 1993; Bayless and others, 2004; Kendall and others, 2005). High human-affected and natural boron concentrations in ground water have been identified by several recent investigations as a possible limitation on water use in parts of the northern Midwestern United States (Rowe, 1999; Ravenscroft and McArthur, 2004; U.S. Environmental Protection Agency, 2007; Zillmer and Fauble, 2004). Leaching of boron from

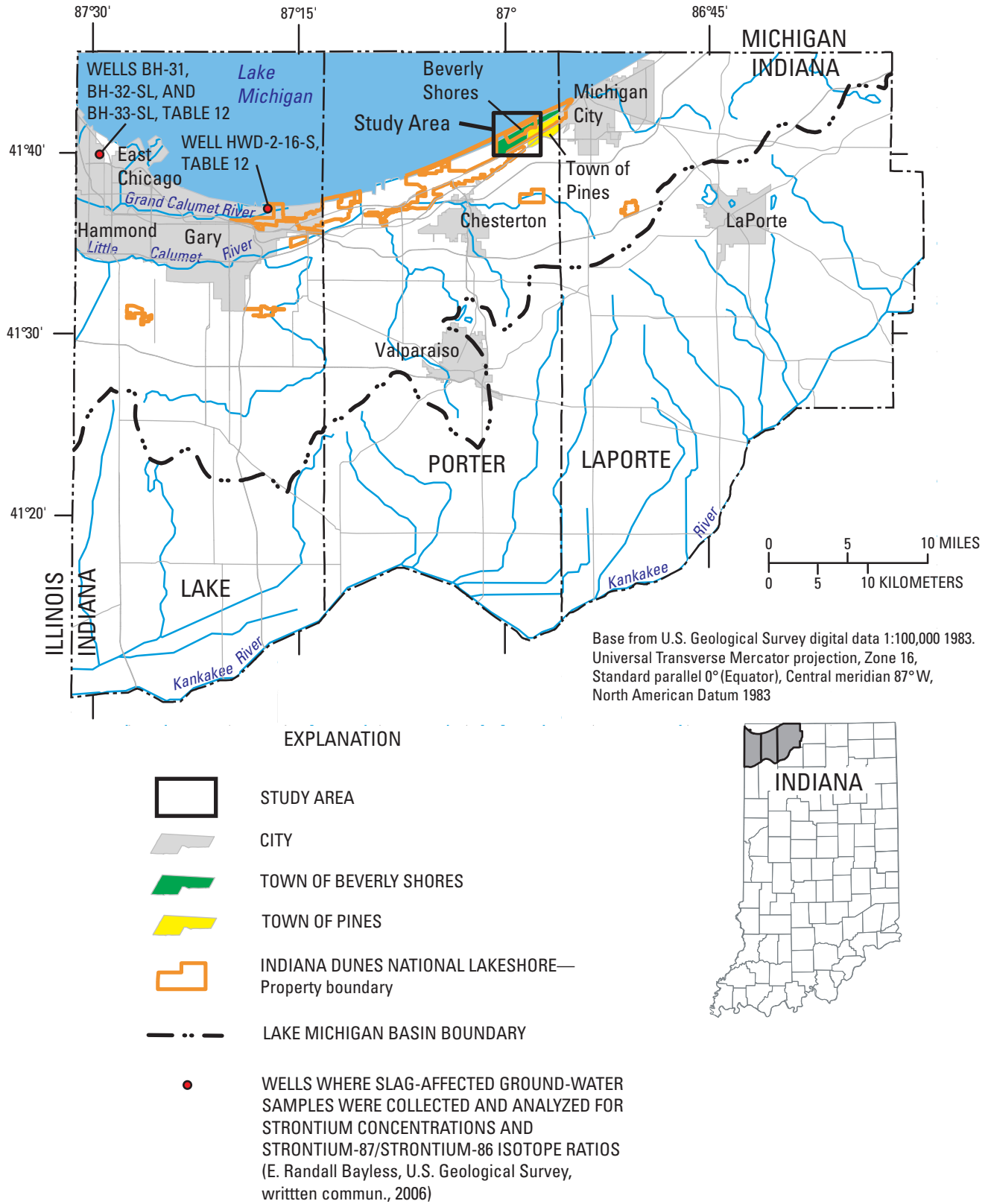


Figure 1. Study area near Beverly Shores and surrounding area, northwestern Indiana.

#### 4 Evaluation of Ground-Water and Boron Sources near Beverly Shores, Northwestern Indiana, 2004

CCP was attributed as the cause of unnaturally large boron concentrations (as large as 186,000  $\mu\text{g/L}$ ) in ground water near uncapped and unlined CCP landfills in Wisconsin (Zillmer and Fauble, 2004) and in ground water (as large as 8,800  $\mu\text{g/L}$ ) downgradient from CCP storage pits in Indiana (Hardy, 1981). Naturally large boron concentrations (as large as 6,100  $\mu\text{g/L}$ ) in ground water from a sandstone and intercalated shale aquifer of northeastern Ingham County, Michigan (Rowe, 1999) were attributed to desorption of boron from Michigan Basin shales as fresh water flushed through a previously saline aquifer (Ravenscroft and McArthur, 2004).

CCP disposal has been a local source of ground- and surface-water contamination in areas east and west of Beverly Shores. A single sample of surface water collected in 1984 from Brown Ditch downstream from the Yard 520 landfill contained concentrations of boron (3,300  $\mu\text{g/L}$ ) and ammonia (2.2 mg/L as N) that were large in comparison to background samples (Hardy, 1984, p. 67, site K3D). Concentrations of trace elements such as boron and molybdenum and major elements such as calcium, magnesium, and sulfate that were higher than typical values in shallow ground water were associated with discharge of CCP-affected water from settling ponds to a nearby stream and to ground water at a site about 5.5 mi west of Beverly Shores (Hardy, 1981). No record exists of CCP use as fill in Beverly Shores before this investigation (Kenneth Theisen, U.S. Environmental Protection Agency, written commun., 2005).

Domestic-wastewater discharges in the Beverly Shores area are also a potential source of boron in ground water. The second largest use of boron worldwide, measured as borate consumption, is in laundry products, in which sodium perborate functions as a whitening agent (Smith, 2002). Boron has been detected in effluent from wastewater-treatment plants (LeBlanc, 1984; Buszka and others, 1994; Vengosh and others, 1994) and septic tanks (Minnesota Pollution Control Agency, 2000). Septic systems equipped with finger- or perforated-tank discharge systems are used for domestic-wastewater discharge in the Beverly Shores area (Olyphant and Harper, 1995). Domestic-wastewater discharge from septic systems is a potential source of nutrients, bacteria, and a variety of synthetic organic compounds (U.S. Environmental Protection Agency, 2004). Although boron concentrations were not reported, domestic-wastewater-affected ground-water quality was indicated by concentrations of chloride and nitrite plus nitrate or ammonia in water from several Beverly Shores area wells (Olyphant and Harper, 1995).

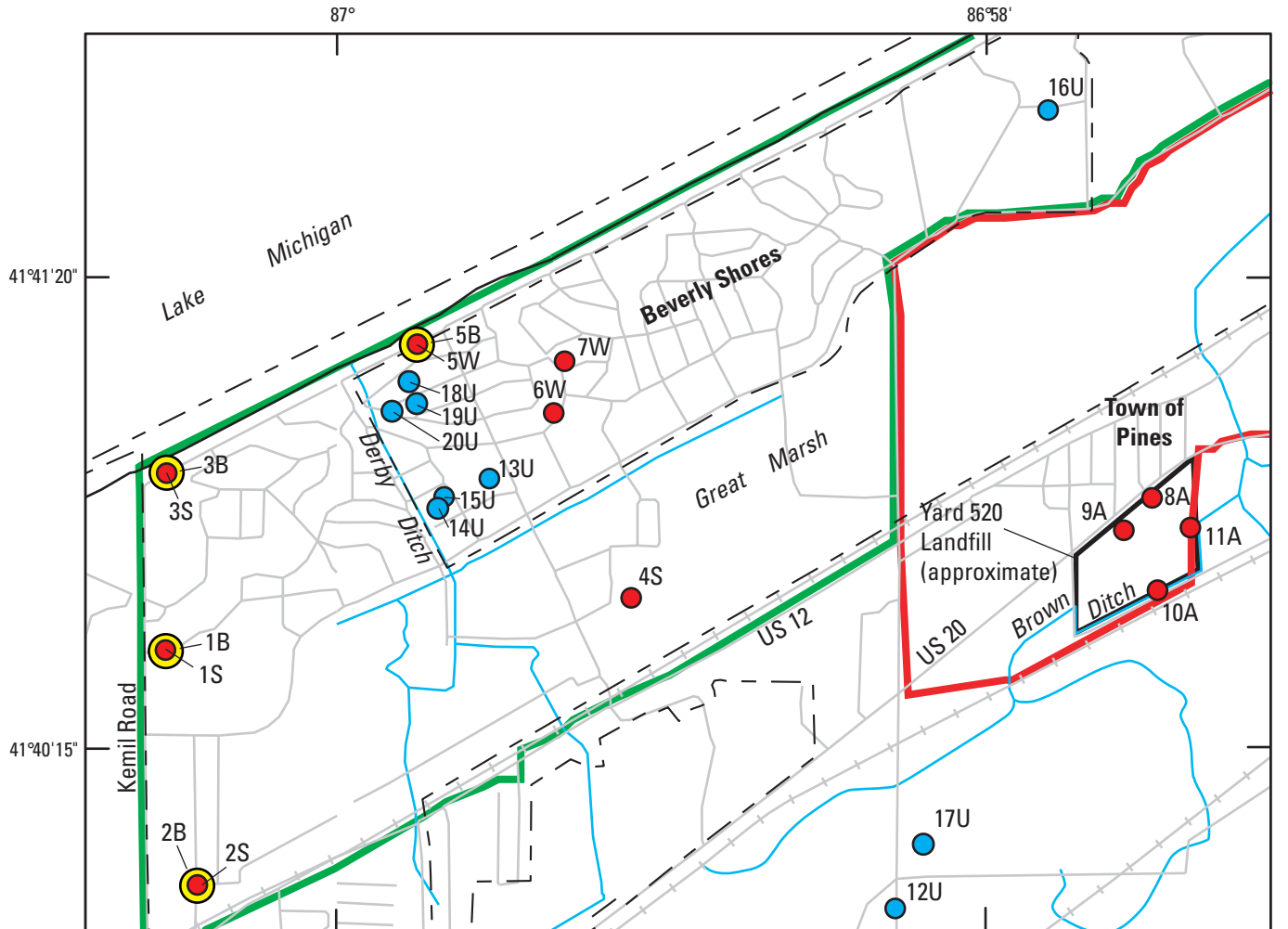
Concentrations of boron in ground water from confined aquifers near Beverly Shores may be naturally larger than those in the mostly unconfined, surficial aquifer (Shedlock and others, 1994). Concentrations of boron were generally larger in 14 water samples from a deep confined aquifer (the basal sand aquifer) and 12 water samples from a shallower confined aquifer (the subfill aquifer) than in 46 water samples from an unconfined sand aquifer (the surficial aquifer) (Shedlock and others, 1994, p. 40–41 and p. 70–82). For example, the median concentration of boron in water from the basal sand aquifer

(730  $\mu\text{g/L}$ ) was larger than the median boron concentrations in water from the subfill aquifer (365  $\mu\text{g/L}$ ) and in water from the surficial aquifer (130  $\mu\text{g/L}$ ) (Shedlock and others, 1994, table 6, p. 42). Because there was some overlap in the distributions of boron in ground water from the basal sand, subfill, and surficial aquifers (Shedlock and others, 1994, p. 40–41), the boron concentration of a sample was not sufficient to indicate whether it was produced from the surficial aquifer or from the basal sand or subfill aquifers. By comparison, the median boron concentration for 574 water samples collected from glacial aquifers in the U.S. from 1991 to 2003 was 28  $\mu\text{g/L}$  (data from National Water-Quality Assessment Data Warehouse; Bell and Williamson, 2006).

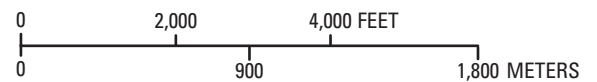
A lack of information to define the screened depth of many wells that produced water with concentrations exceeding a RAL precluded identification of whether the ground-water source for those wells was the surficial aquifer, or the subfill aquifer, or basal sand aquifer. For example, no well logs were available for the three private wells and the one elementary school well sampled by the USEPA in 2004. Few records exist in the files of the Indiana Department of Natural Resources –Water Well Record database (Indiana Department of Natural Resources, 2007) for private and public-supply wells in the Beverly Shores and Town of Pines areas because most residences were built and wells drilled before the State required submission of water-well logs in 1987 (Indiana Legislative Services Agency, undated). Access to the wells for direct measurements of depth and camera observations of the well screen was limited by sealed casings, the need to remove and reinstall submersible pumps, wiring, and plumbing from each well (requiring the assistance of a licensed plumber or water well contractor), and the difficulty in obtaining the homeowner's permission. When well data were not available, the well was referred to as a "well with an unknown ground-water source". Other methods were needed to indicate whether the sources of boron in ground-water samples were natural or human affected.

Differences in the abundance of  $^{11}\text{B}$  (boron-11) and  $^{10}\text{B}$  (boron-10) in ground-water samples relative to the ratio in a standard material (the B stable-isotope ratio or  $\delta^{11}\text{B}$ ) may be useful in distinguishing the sources of boron in ground-water samples (Vengosh and others, 1994; Buszka and others, 1994; Bassett and others, 1995). Boron has two naturally-occurring stable isotopes, a  $^{11}\text{B}$  isotope with five protons and six neutrons (boron-11 or  $^{11}\text{B}$ ) and a  $^{10}\text{B}$  isotope with five protons and five neutrons. The environmental abundance of  $^{11}\text{B}$  is about 80.1 percent and that of  $^{10}\text{B}$  is about 19.9 percent (Kendall and others, 2005). The stable-isotope ratio of boron in leachate from CCP (fly ash) can differ greatly from that in natural ground water (Davidson and Bassett, 1993). Boron isotopes have been used to distinguish water affected by detergent residues (Barth, 1998; Seiler, 2005; Verstraeten and others, 2005), treated municipal wastewater, and saline ground water (Vengosh and others, 1994; Leenhouts and others, 1998; Buszka and others, 1994; Bassett and others, 1995). Several of those investigators (Vengosh and others, 1994; Seiler, 2005;





Base from U.S. Geological Survey digital data 1:100,000 1983. Universal Transverse Mercator projection, Zone 16, Standard parallel 0° (Equator), Central meridian 87°W, North American Datum 1983



EXPLANATION

- INDIANA DUNES NATIONAL LAKESHORE— Approximate park boundary
- BEVERLY SHORES, Approximate town limit
- TOWN OF PINES, Approximate town limit
- ROAD
- STREAM
- LAKE MICHIGAN SHORELINE— Approximate location
- 4S WELL IN SURFICIAL AQUIFER—With project well identifier. Letters following number indicate known or likely source of water:  
A, Coal-combustion product affected water  
S, Water not affected by potential boron source  
W, Water affected by domestic wastewater
- 2B WELL IN BASAL SAND AQUIFER—With project well identifier
- 12U WELL WITH UNKNOWN GROUND-WATER SOURCE— With project well identifier

**Figure 2.** Wells sampled in the study area near Beverly Shores, the Town of Pines, and the Indiana Dunes National Lakeshore, northwestern Indiana, 2004.

Buszka and others, 1994; Bassett and others, 1995) used water samples with known or suspected contaminant sources to define typical concentrations of boron and boron stable isotopes for each representative source of boron. Hypothetical mixtures between those potential sources were used to identify the possible sources of boron in other samples from areas with unknown sources of boron.

Confined aquifers in northern Porter County are less susceptible to contamination, depending on the thickness of confining silt and clay layers (Beaty, 1994); boron in water from a confined aquifer is therefore more likely to represent natural sources if its source of recharge predates the source of contamination. Tritium concentrations have been used in northwestern Indiana to distinguish between older and younger ground water (Kay and others, 2002; Hasenmueller and others, 2001; Shedlock and others, 1993). Tritium is a radioactive isotope of hydrogen (hydrogen-3) with an atomic mass of 3 and a half-life of 12.3 years. Tritium is much less abundant in nature than hydrogen; there are naturally about  $10^{18}$  hydrogen atoms for each tritium atom. Synthetic tritium was introduced to the atmosphere in large amounts by atmospheric nuclear testing between 1952 and 1980 (Clark and Fritz, 1997); the difference between lower pre-test and larger post-test tritium concentrations in water is used to indicate differences in the relative ground-water age. Very low tritium concentrations in water from the subsoil aquifer (0.3 to 1.6 tritium units or TU, four samples) and much larger concentrations in water from the surficial aquifer (36 and 47 TU, two samples) were previously identified about 4.5 mi west of the study area (Shedlock and others, 1993). Tritium concentrations were used to identify mixtures between confined ground water from the subsoil aquifer and ground water affected by infiltrating precipitation (53 TU, average of 1978-1979 precipitation data from Chicago, Ill., International Atomic Energy Agency, 2006; Shedlock and others, 1993).

A geochemically-based classification of the source of boron in ground water could potentially identify the similarity of boron in a water sample to potential sources or mixtures between potential sources or whether the relative age of ground water predated the potential sources of contamination. A geochemical classification of boron source would have the advantage of limiting the need to remove and reinstall well plumbing and pumps for direct, camera-based observations of well depth and screen interval. No previous analyses of boron isotope ratios in CCP-affected ground water, domestic-wastewater-affected ground water, and potential natural ground-water sources (surficial and basal sand aquifers) had been reported for the study area before this investigation. To evaluate the application of boron isotopes and tritium data in indicating potential sources of boron in ground water, it was necessary to collect and analyze samples of those representative ground-water sources. Data were also needed from the immediate area of study to validate the use of tritium as a characteristic to distinguish relatively younger ground water from shallow aquifers and relatively older ground water from confined aquifers.

## Purpose and Scope

This report describes the results of an investigation by the U.S. Geological Survey, in cooperation with the U.S. Environmental Protection Agency, Region 5, to evaluate the use of boron stable isotopes and concentrations of boron, tritium, and other constituents in classifying possible sources of boron in ground water near Beverly Shores, Indiana. The evaluation focused on whether these geochemical characteristics in ground water could be used to distinguish between natural and human-affected sources of boron in ground water.

Ground-water samples were collected by the USGS and the USEPA from March through May 2004 from 15 wells that have water quality representative of four potential sources of boron in ground water. Those representative sources are CCP-affected water from a surficial aquifer (four wells); domestic-wastewater-affected water from a surficial aquifer (three wells); water from parts of a surficial aquifer distant from human-affected boron sources (surficial aquifer) (four wells); and water from a deep, confined aquifer (the basal sand aquifer) representing natural boron sources (four wells). Water samples also were collected in April and November 2004 from eight private, domestic-supply wells and from one public-supply well where there was no well log available, no depth information and no way to readily access the wells, measure the well depth and screen interval, and determine the source of ground water. Ground-water samples were chemically analyzed to describe the water chemistry of boron and its major stable isotopes, tritium, and other water-chemistry constituents. Molybdenum was not analyzed in water samples collected by this study.

The data were evaluated for their potential to chemically distinguish between natural (surficial aquifer wells distant from human-affected boron sources and basal sand aquifer) and human-affected sources of contaminants (CCP affected surficial-aquifer water and domestic-wastewater-affected surficial-aquifer water). A secondary evaluation used the tritium analyses to determine approximate time since recharge; this would distinguish between ground water from the surficial aquifer and from deeper, confined aquifers less susceptible to human-affected contamination. The chemical differences were used to classify the likely source of boron in other ground-water samples from the Beverly Shores area where the ground-water source was not known. The classifications of boron source were compared with other constituent data (concentrations of strontium, chloride, nitrate, and ammonia) and the ratio of the stable isotopes strontium-87/strontium-86. This report provides information about the sampled wells and their relation to potential local sources of boron, the sampling and analytical methods used to describe ground-water chemistry, and an analysis of the chemical similarities between ground-water samples and water samples that represent potential boron sources.

## Description of the Study Area

The study area was about 5.8 mi<sup>2</sup> in northeastern Porter County, northwestern Indiana (fig. 1). The investigation focused on areas within and south of Beverly Shores between Kemil Road to the west and extending eastward to include the Yard 520 landfill near the Town of Pines (fig. 2). As of the 2000 census, the population of Beverly Shores was 708 (U.S. Census Bureau, 2007). The study area also included parts of areas drained by Derby Ditch near Beverly Shores and Brown Ditch near the Town of Pines. Both streams drain local areas and wetlands and discharge to Lake Michigan. The Great Marsh, a major local interdunal wetland, crosses the central part of the study area from northeast to southwest (fig. 3).

During 2004 and parts of 2005, single-family residences in the study area mainly obtained water from domestic wells and disposed of domestic wastewater through septic systems. Domestic wells in the Beverly Shores area drew ground water from shallow wells developed in an unconfined surficial aquifer with depths less than about 60 to 70 ft below land surface and from deeper wells (Olyphant and Harper, 1995) that may be developed in confined sand or sand and gravel aquifers. During 2005, residences in parts of Beverly Shores were connected to water supplied from a Lake Michigan intake by a pipeline from Michigan City.

Land use in the study area is principally residential along streets in Beverly Shores and Pines and is a mixture of residential and commercial uses along major roads (US 12 and US 20). Principal transportation land uses that cross the study area include US 12, US 20, several paved and unpaved roads, and railroads. Transportation-related potential sources of contaminants may include highway runoff, deicers, and spills of materials transported along roadways or railroads (U.S. Environmental Protection Agency, 2004; Watson and others, 2002). Parts of the study area within the Indiana Dunes National Lakeshore and adjacent parkland are maintained as natural and restored wetlands and wooded dune and swale environments.

## Hydrogeologic Framework

The hydrogeologic framework (table 1) and regional directions of ground-water flow defined by Shedlock and others (1994) were the basis used to interpret the locations of water samples collected for this investigation within regional, intermediate, and local ground-water-flow systems. This hydrogeologic framework relates to the one described by Beaty (1994) for regional aquifer systems of the Lake Michigan region (table 1). Ground-water resources in the study area described by Beaty (1994) chiefly include two regionally important, unconsolidated aquifer systems (the Calumet aquifer system and the Lacustrine Plain aquifer system) (fig. 4) and one underlying bedrock aquifer system (the Silurian-Devonian Carbonate aquifer system). The Calumet and Lacustrine Plain aquifer systems are the most extensively used for ground-water withdrawals by residences and for

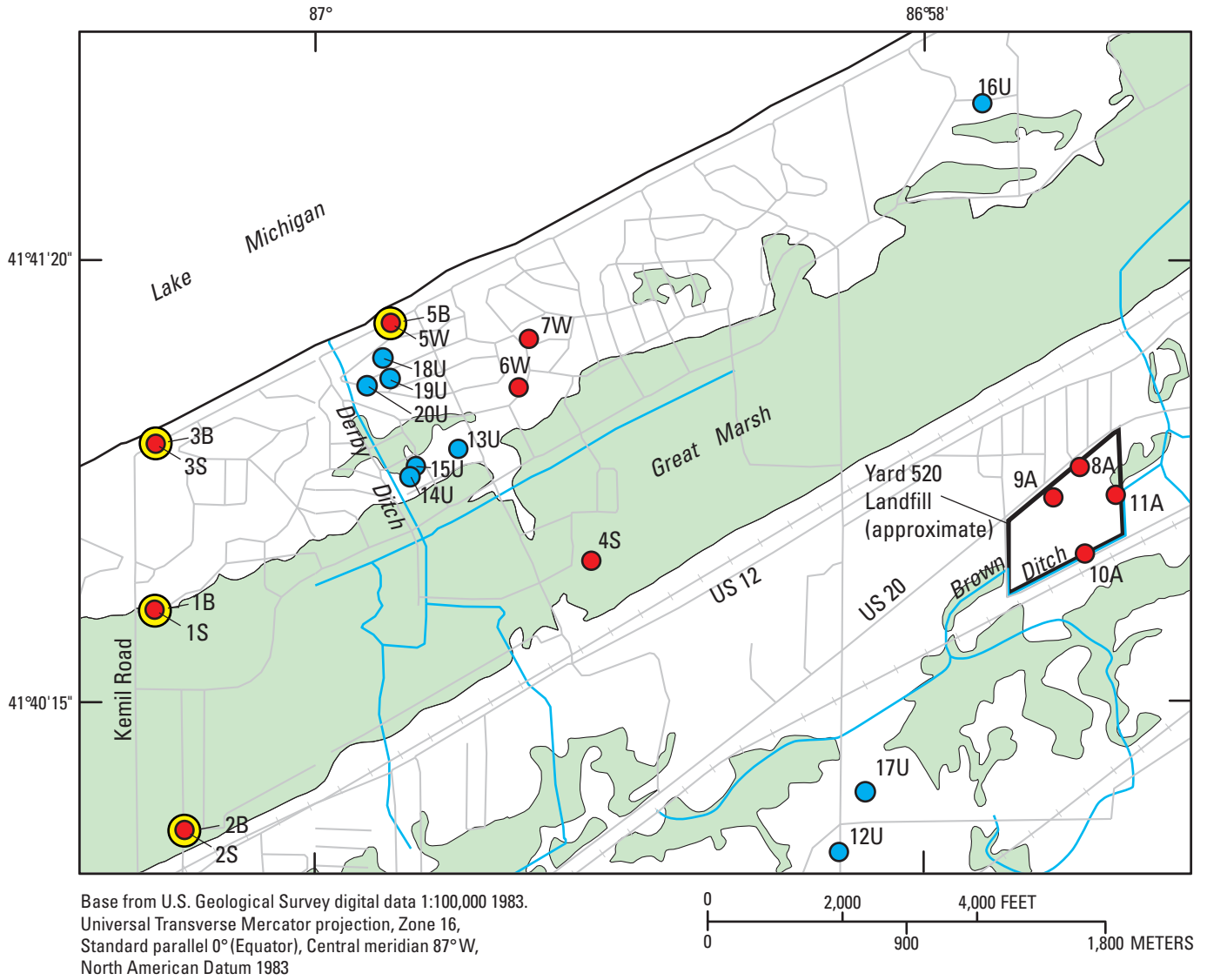
public supply in the area. The hydrogeologic framework of the Beverly Shores area of Porter County in northwestern Indiana consists of three glacial aquifers, the surficial aquifer, the sub-till aquifer, and the basal sand aquifer, separated by variable thicknesses of glacial till and lacustrine clay and silt (fig. 5). The remainder of this section presents the relation of the aquifers described by Shedlock and others (1994) to the regional aquifer systems of Beaty (1994). A more extensive comparison with frameworks used by other authors is presented in Shedlock and others (1994).

The uppermost aquifer, known locally as the surficial aquifer (abbreviated as SA in later parts of this report), consists of fine-to-medium grained dune, beach, and lacustrine sands and gravels (Beaty, 1994; Thompson, 1987). For this report, the Calumet aquifer system in the Lake Michigan region (Beaty, 1994) is assumed as equivalent to the surficial aquifer. The saturated thickness of the surficial aquifer ranges from about 5 ft along the Lake Michigan shoreline to 30 to 35 ft in the areas south of Beverly Shores near highways US 12 (Watson and others, 2002) and US 20 (Shedlock and others, 1994, fig. 9, p. 25) and near areas drained by Derby Ditch. The surficial aquifer generally is unconfined but can be confined in small areas by interlaminated silt and clay, marls, calcareous mud, and peat deposits (Shedlock and others, 1994, p. 17). The aquifer is highly susceptible to contamination from land surface sources because of this lack of confinement (Beaty, 1994).

The sub-till aquifer in the study area is a series of sand units with interbedded lenses of clay that underlies the surficial aquifer and confining units beneath the Lake Border moraine (fig. 5), principally south of the area between highways US 12 and US 20. The saturated thickness of the sub-till aquifer in the study area ranges from not present to about 80 ft near US 20 (Shedlock and others, 1994, fig. 22, p. 52). A deeper, confined sand aquifer, known as the basal sand aquifer, consists of discontinuous lenses of sand and gravel interbedded with layers of silt and clay at or near the base of unconsolidated glacial deposits where they contact the bedrock. Confining units of interbedded till and glacial lacustrine clay and silt separate the surficial aquifer from the underlying sub-till aquifer and the sub-till aquifer from the basal sand aquifer. Wells that flow at land surface have been identified in part of the basal sand aquifer in the study area (Shedlock and others, 1994, p. 21). The sub-till and basal sand aquifers (table 1) are assumed to be equivalent to the Lacustrine Plain aquifer system of Beaty (1994).

Bedrock in the study area is described mostly as Devonian shale and Silurian carbonate lithologies (Shedlock and others, 1994, fig. 8, p. 22). Water from the bedrock aquifer may be the predominant source of water to some wells in the study area, though no known bedrock aquifer wells were available to sample for this investigation. The Silurian-Devonian carbonate aquifer system in the Lake Michigan region (Beaty, 1994) is assumed as equivalent to the bedrock aquifer for this report (table 1).

8 Evaluation of Ground-Water and Boron Sources near Beverly Shores, Northwestern Indiana, 2004



EXPLANATION







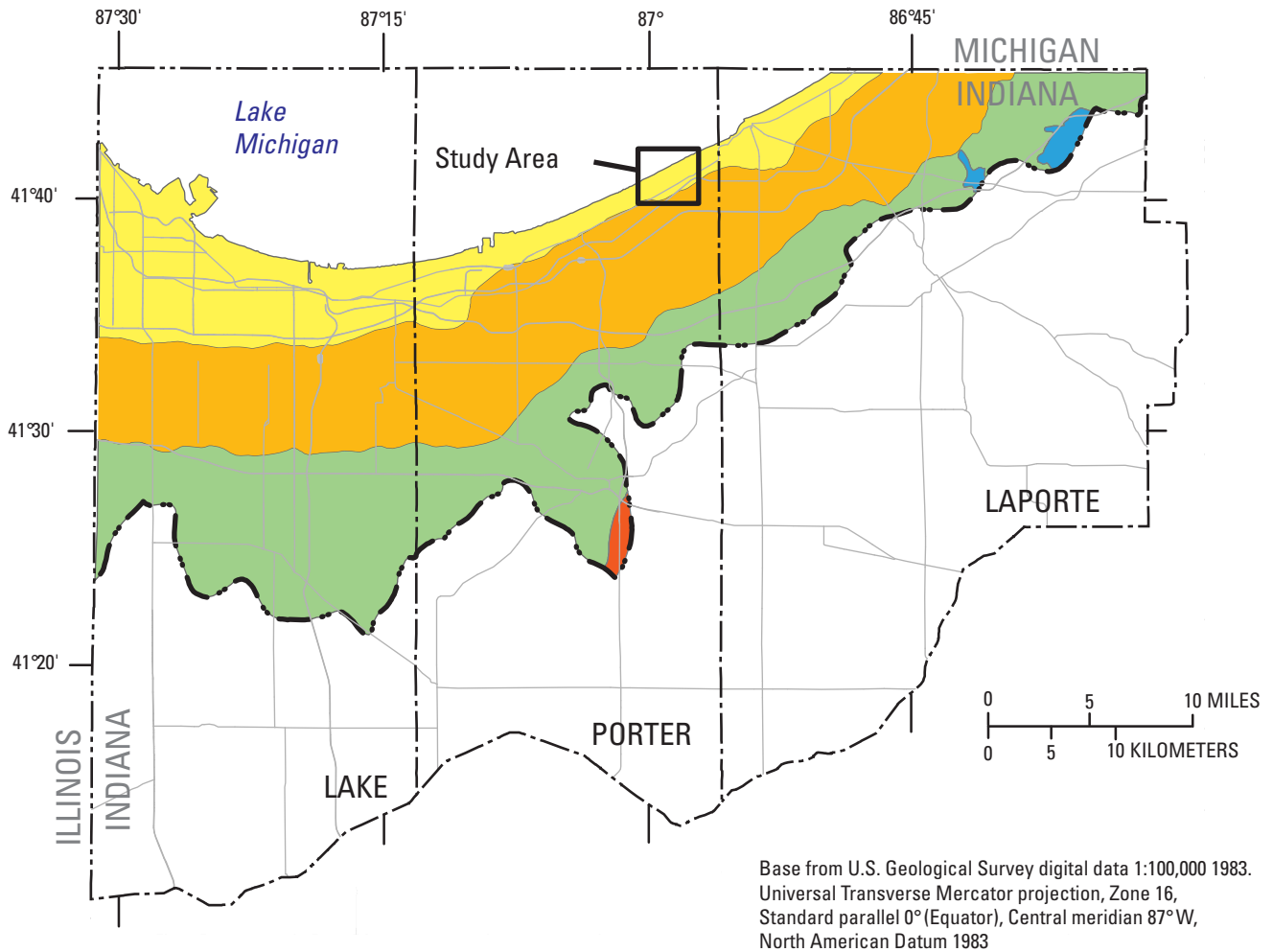
- |   |              |   |     |  |
|---|--------------|---|-----|--|
|  | WETLAND AREA |  | 4S  | WELL IN SURFICIAL AQUIFER—With project well identifier. Letters following number indicate known or likely source of water:<br>A, Coal-combustion product affected water<br>S, Water not affected by potential boron source<br>W, Water affected by domestic wastewater |
|  | ROAD         |  | 2B  | WELL IN BASAL SAND AQUIFER—With project well identifier  |
|  | STREAM       |  | 12U | WELL WITH UNKNOWN GROUND-WATER SOURCE—With project well identifier   |

Figure 3. Wells sampled and wetland areas in the study area near Beverly Shores, northwestern Indiana, 2004.



EXPLANATION

AQUIFER SYSTEMS OF THE LAKE MICHIGAN BASIN—  
Approximate extent as mapped by Beaty (1994)

- CALUMET AQUIFER SYSTEM
- LACUSTRINE PLAIN AQUIFER SYSTEM
- VALPARAISO MORAINE AQUIFER SYSTEM
- KANKAKEE AQUIFER SYSTEM
- VALPARAISO APRON AQUIFER SYSTEM
- STUDY AREA
- LAKE MICHIGAN BASIN BOUNDARY

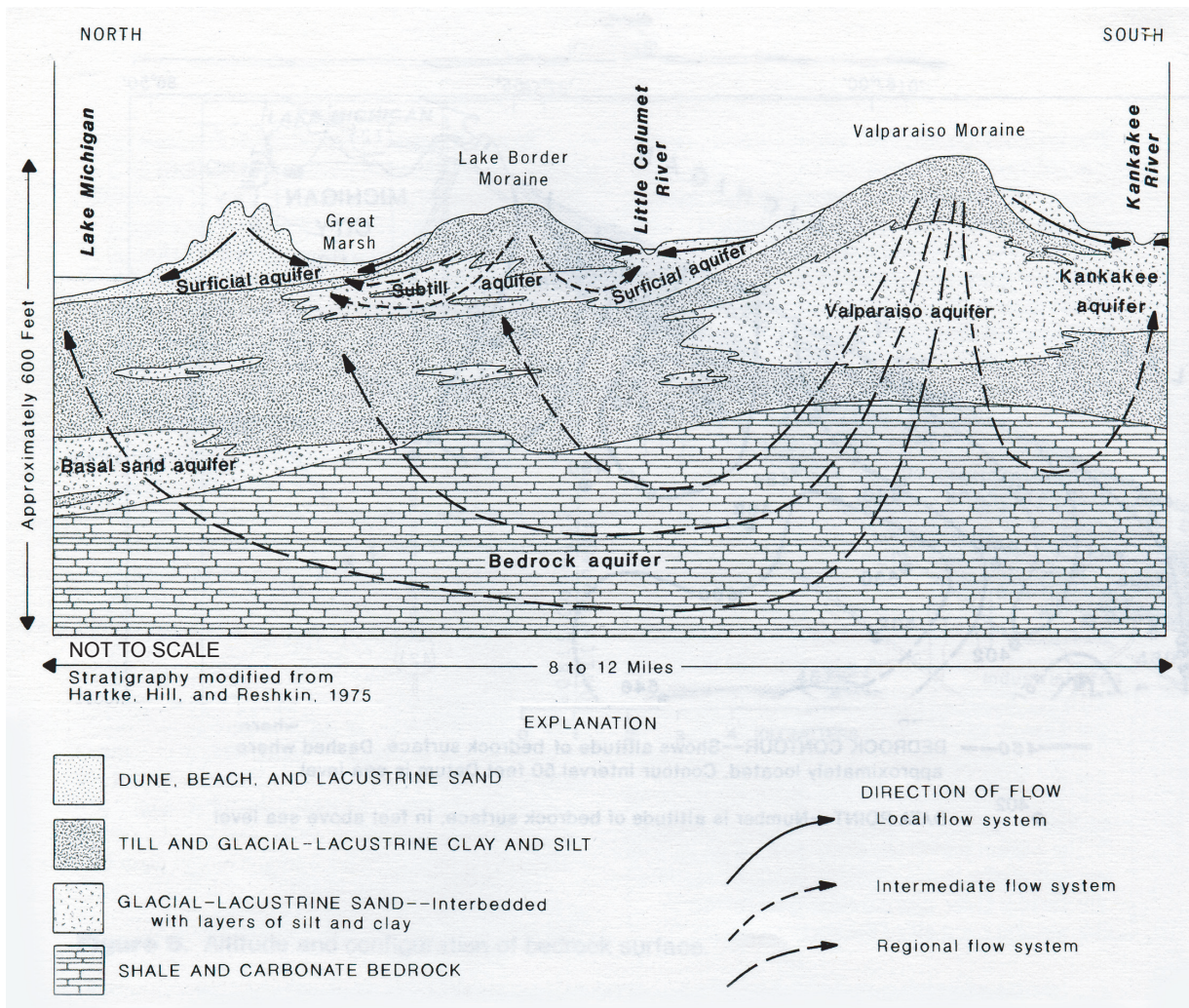
**Figure 4.** Unconsolidated aquifer systems in the Lake Michigan region and the study area near Beverly Shores, northwestern Indiana (Definitions of aquifer system characteristics can be found in Beaty, 1994, plate 2).

The ground-water-flow system is assumed to be at steady state in the study area (fig. 5). Although no quantitative evaluation of changes in water use was done in the intervening period between the framework being defined (Shedlock and others, 1994) and this investigation (2004), no large-scale changes in development of the area were observed that would correspond to changes in ground-water production and flow directions.

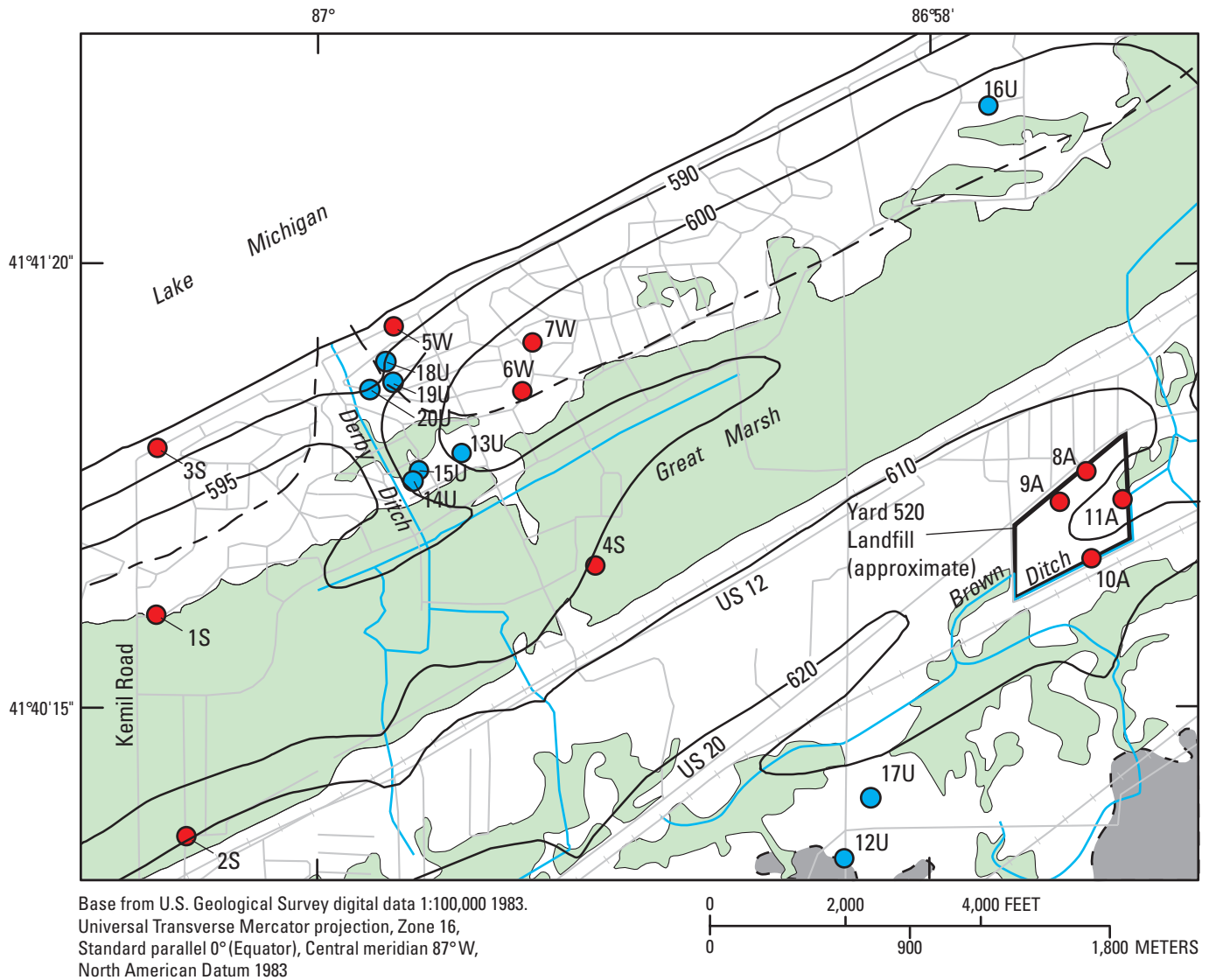
Local flow systems in the surficial aquifer are recharged by infiltration into the permeable dune-beach complex sands and, to a lesser extent, by upward flow from the subfill and deeper aquifers (fig. 5). Discharge from the surficial aquifer is along streams, manmade ditches, and wetlands (Shedlock and others, 1994) and through domestic and other wells. The October 1980 altitude of the water table in the surficial aquifer indicates ground-water discharge from the surficial aquifer to the Great Marsh and its drainages and to Lake Michigan (fig. 6). This steady-state direction of flow, from higher water-table elevations near dune ridges and toward discharge areas

in wetlands, was valid at a site in the study area along US 12 from 1994 to 1997 (Watson and others, 2002).









Intermediate flow systems of the subfill aquifer are recharged by infiltration near the Lake Border Moraine and, to a lesser extent, by upward flow through the confining unit from the bedrock (fig. 5). The basal sand aquifer most likely is recharged along the Valparaiso Moraine south of the study area. Ground water from the Valparaiso Moraine area flows downward into and through the bedrock aquifer and most likely discharges to the subfill aquifer and the basal sand aquifer (fig. 5). Some parts of the study area are a regional discharge zone for the basal sand aquifer; water from the basal sand aquifer is assumed to discharge to Lake Michigan and to the surficial aquifer through the confining unit. Flowing wells in areas within the study area and north of US 12 and the Lake Border Moraine indicate the potential for water from the basal sand aquifer to flow naturally through the confining unit and discharge into the surficial aquifer of the Beverly Shores area (Shedlock and others, 1994, p. 21).



**Figure 5.** Diagrammatic hydrogeologic section showing aquifers and conceptual ground-water-flow directions in the western half of the Indiana Dunes National Lakeshore near Beverly Shores, Indiana (diagram reproduced from Shedlock and others, 1994, fig. 7, p. 21).



EXPLANATION

-  APPROXIMATE EXTENT WHERE SURFICIAL AQUIFER IS ABSENT
-  WETLAND AREA
-  600 WATER-TABLE CONTOUR—Shows approximate altitude of the water table in the surficial aquifer, October 1980. Contours are in feet above National Geodetic Vertical Datum of 1929. Contour interval varies
-  APPROXIMATE WATER-TABLE DIVIDE, OCTOBER 1980
-  ROAD
-  STREAM
-  4S WELL IN SURFICIAL AQUIFER—With project well identifier. Letters following number indicate known or likely source of water:  
A, Coal-combustion product affected water  
S, Water not affected by potential boron source  
W, Water affected by domestic wastewater
-  12U WELL WITH UNKNOWN GROUND-WATER SOURCE—With project well identifier

**Figure 6.** Wells completed in the surficial aquifer and wells with an unknown ground-water source sampled near Beverly Shores, northwestern Indiana, 2004, in relation to the water-table altitude in the surficial aquifer, October 1980 (Shedlock and others, 1994, p. 34-35).

**Table 1.** Comparison of hydrogeologic framework of the study area near Beverly Shores, Indiana with those of previous investigations.

Lithostratigraphic descriptions	Hydrogeologic framework designation	
	This report and Shedlock and others (1994)	Beaty (1994)
Fine-to-medium grained dune, beach and lacustrine sands and gravels (Holocene and Pleistocene age)	Surficial aquifer (SA)	Calumet aquifer system
Glacial and lacustrine sands of Pleistocene age, with interbedded clays and silts, including tills of the Lake Border Moraine	Confining units	Lacustrine Plain aquifer system
	Subtill aquifer	
	Confining units	
	Basal sand aquifer	
Shale and carbonate rocks of Devonian and Silurian age	Bedrock aquifer	Silurian-Devonian carbonate aquifer system

## Methods of Data Collection and Analysis

Water samples were collected from 20 wells, March through May 2004, and from 4 additional wells in November 2004. This section describes the methods used to select wells for sampling, develop wells before sampling, collect ground-water samples, and perform chemical analyses on those samples. Quality-assurance procedures used to validate water-chemistry data are described.

### Well Selection

Wells sampled to classify possible sources of boron principally were selected according to two criteria: (1) whether the wells were screened in the surficial aquifer or the basal sand aquifer and (2) the proximity or geochemical similarity of water from surficial aquifer wells to potential sources of boron (CCP or domestic-wastewater disposal). These sampled wells were adjacent to or were wells with a known total well depth based on a well-driller's log or a previous report that evaluated the producing aquifer and a previous ground-water-quality analysis (Shedlock and others, 1994; Olyphant and Harper, 1995). The sampled wells were categorized into five groups.

### Surficial Aquifer Wells Distant from Human-Affected Boron Sources

This group consisted of four USGS wells: 1S, 2S, 3S, and 4S (table 2, fig. 2). All except well 3S were in or adjacent to the Great Marsh (fig. 3) and geochemically unaffected by potential human-affected boron sources. Well 3S was northwest of a beach home along a dune ridge and overlooked the Lake Michigan shore (fig. 7). All four wells initially were con-

sidered to be unaffected by domestic-wastewater drainage or CCP leachate. Water from wells 3S and 4S and from shallow wells next to wells 1S and 2S had low specific conductivity values in previous analyses (Shedlock and others, 1994). Wells 1S, 2S, 3S, and 4S were sampled to represent ambient water quality and natural sources of boron in ground water from local flow systems in the surficial aquifer.

### Basal Sand Aquifer Wells Representing Natural Boron Sources

This group of sampled wells consisted of three USGS wells 1B, 2B, and 3B and one well 5B at a National Park Service (NPS) rest room facility. The wells were screened in the basal sand aquifer (table 2, fig. 2). These wells flowed at land surface when opened to the atmosphere; an example of a local flowing well is shown in figure 8. Water from the basal sand aquifer in the study area represents natural sources of boron within the regional flow system.

### Coal-Combustion-Product-Affected Wells in the Surficial Aquifer

This potential source of boron was represented by collecting samples from four previously sampled wells suspected to be affected by CCP leachate. The four observation wells (8A, 9A, 10A, and 11A) were sampled at a former CCP disposal site, the Yard 520 landfill near Pines (figs. 2 and 9; table 2). Larger specific conductance, boron, and sulfate concentrations were found in previous samples from wells at the Yard 520 landfill in relation to other area wells (Kenneth Theisen, U.S. Environmental Protection Agency, written commun., 2004).



**Table 2.** Selected characteristics of wells sampled for water chemistry near Beverly Shores and the Town of Pines, northwestern Indiana, 2004.

[USGS, U.S. Geological Survey; Latitude and longitude symbols: °, degrees; ', minutes; ", seconds; >, greater than; —, no data or not measured; horizontal datum is North American Datum of 1983]

Project well identifier (figure 2)	USGS station identification number	Well name	Latitude (degrees, minutes, and seconds)	Longitude (degrees, minutes, and seconds)	Depth (feet below land surface)
Surficial aquifer wells distant from human-affected boron sources					
1S	414029087003204	305B-7	41° 40' 28.11"	87° 00' 31.53"	6.95
2S	413957087002603	211-9	41° 39' 56.37"	87° 00' 25.70"	8.8
3S	414057087003003	212-24	41° 40' 53.02"	87° 00' 31.34"	23.05
4S	414036086590601	GM-24	41° 40' 35.85"	86° 59' 06.09"	6.91
Basal sand aquifer wells representing natural boron sources					
1B	414029087003201	305-156	41° 40' 28.68"	87° 00' 31.58"	153.5
2B	413957087002601	211-178	41° 39' 56.37"	87° 00' 25.70"	163.5
3B	414057087003000	212-212	41° 40' 53.02"	87° 00' 31.34"	211.5
5B	414111086594501	Lakeview Beach Deep	41° 41' 10.76"	86° 59' 45.30"	187
Coal-combustion product affected wells in the surficial aquifer					
8A	414050086573001	Yard 520 well MW-6	41° 40' 49.59"	86° 57' 30.46"	35
9A	414045086573601	Yard 520 well TW-12	41° 40' 45.12"	86° 57' 35.63"	32.65
10A	414037086572901	Yard 520 well MW-3	41° 40' 36.89"	86° 57' 29.46"	17
11A	414046086572301	Yard 520 well MW-8	41° 40' 45.52"	86° 57' 23.43"	18.12
Domestic-wastewater-affected wells in the surficial aquifer					
5W	414111086594502	Lakeview Beach Shallow	41° 41' 10.76"	86° 59' 45.30"	36
6W	414101086592001	Domestic-water supply, Beverly Shores area	41° 41' 01.30"	86° 59' 20.30"	62
7W	414108086591801	Domestic-water supply, Beverly Shores area (next door to well 60 of Olyphant and Harper, 1995)	41° 41' 08.41"	86° 59' 18.27"	<sup>1</sup> 39
Wells with an unknown ground-water source					
12U	413953086581801	Public-water supply at an elementary school, Town of Pines area	41° 39' 53.11"	86° 58' 17.62"	<sup>2</sup> >100
13U	414052086593201	Domestic-water supply, Beverly Shores area	41° 40' 52.29"	86° 59' 32.06"	<sup>3</sup> 65
14U	414048086594201	Domestic-water supply, Beverly Shores area	41° 40' 48.23"	86° 59' 41.59"	—
15U	414050086594001	Domestic-water supply, Beverly Shores area	41° 40' 49.76"	86° 59' 40.40"	<sup>2</sup> 246
16U	414143086574901	Domestic-water supply, Beverly Shores area	41° 41' 42.96"	86° 57' 49.49"	—
17U	414002086581301	Domestic-water supply, Town of Pines area	41° 40' 02.01"	86° 58' 12.53"	—
18U	414106086594701	Domestic-water supply, Beverly Shores area	41° 41' 05.65"	86° 59' 46.84"	—
19U	414102086595001	Domestic-water supply, Beverly Shores area	41° 41' 01.55"	86° 59' 49.98"	—
20U	414103086594501	Domestic-water supply, Beverly Shores area	41° 41' 02.62"	86° 59' 45.47"	<sup>2</sup> 200

<sup>1</sup>May be depth of pump.

<sup>2</sup>Information about well depth not determined until after samples were collected. Based on well depth, producing aquifer was classified as follows: well 12U, subtidal aquifer; well 13U, surficial aquifer; and wells 15U and 20U, basal sand aquifer.



**Figure 7.** Wells 3S and 3B in relation to a nearby home along a dune ridge, facing southeast at Beverly Shores, Indiana (Photograph by Lee R. Watson, U.S. Geological Survey, March 28, 2005).

### Domestic-Wastewater-Affected Wells in the Surficial Aquifer

Three wells near Beverly Shores were sampled to represent domestic-wastewater-affected ground water. Total depths of one private domestic well (7W, fig. 2) and one NPS well (5W; figs. 2 and 10) indicated the surficial aquifer as the ground-water source; concentrations of chloride and nitrate from previous analyses indicated potential domestic-wastewa-

ter-affected water quality (Olyphant and Harper, 1995; Susan Lehman, National Park Service, written commun., 2004). Elevated concentrations of nitrate and ammonia are characteristic of domestic-wastewater contamination from septic systems (Robertson and Blowes, 1995; Robertson and others, 1991; Minnesota Pollution Control Agency, 2000). A third well (6W) was on property adjacent to a well that produced from the surficial aquifer with large concentrations of chloride and ammonia (well 60, depth 65 ft; Olyphant and Harper,

1995); the owner of well 6W indicated the well was 62 ft deep (table 2). Large concentrations of chloride associated with large ammonia concentrations can indicate the presence of water-softener-affected wastewater (Panno and others, 2006). The local presence of domestic-wastewater contamination was indicated by observation of a suspected domestic-wastewater seep (fig. 11).

### Water Samples from Wells with an Unknown Ground-Water Source

Eight residential wells (13U—20U) and one well (12U) used for public-water supply at an elementary school were identified by the USEPA as wells that could have concentrations of boron that were close to or exceeded the RAL (Kenneth Theisen, U.S. Environmental Protection Agency, written commun., 2006). These wells had no available well log and no owner permissions to access the well to measure well depth and screened interval. Because the ground-water source to

each well could not be determined, they were described as “wells with an unknown ground-water source”. These wells were sampled to determine whether values of boron isotope ratios, and concentrations of boron, tritium, and other chemical constituents would allow identification of the source of boron in local ground water when the ground-water source was not known.

After water samples were collected in 2004, additional depth information was identified for wells 12U, 13U, 15U, and 20U (table 2) by a closer examination of data from prior interviews with well owners (Christopher Carlson, Wisconsin Department of Natural Resources, written commun., 2004). Assuming that these depths represented the bottom of the well screen interval, the ground-water sources to these wells were tentatively classified as follows: 12U, subsoil aquifer; 13U surficial aquifer, 15U and 20U, basal sand aquifer (table 2). Data from these four wells were used to independently validate whether chemically based interpretations of ground-water source agreed with the well-depth-based interpretations.



**Figure 8.** A flowing well developed in the basal sand aquifer at Beverly Shores, Indiana (Photograph by Lee R. Watson, U.S. Geological Survey, March 28, 2005).

## Sampling Methods

Samples from observation wells open to the surficial aquifer (1S, 2S, 3S, 4S, 8A, 9A, 10A, 11A, and 5W) and the basal sand aquifer (1B, 2B, and 3B) (table 2) were collected after at least three well volumes were purged from the well with submersible sampling pumps. The NPS well (5B); a public-supply well (12U); and domestic wells 13U, 14U, and 16U through 19U were equipped with submersible pumps and plumbing; hence, samples were collected from faucets at the wellhead or at the home exterior. Well owners of wells 5B, 12U through 14U and 16U through 19U indicated that the sampled faucets produced untreated ground water. Samples from wells 15U and 20U were collected directly from the casing overflow; water from both wells flowed continuously at land surface at about 1 L/min or less.

Before each well was sampled, equipment was cleaned by use of a sequential rinse with (1) a dilute solution of laboratory-grade, non-phosphate detergent and tap water; (2) tap water; and (3) deionized water. Before use each sampling day,

the multiparameter water-quality meter was calibrated, using laboratory-grade calibration solutions and following manufacturer's procedures and protocols (U.S. Geological Survey, variously dated). Performance of the portable nephelometric turbidimeter was checked daily, using standard cells and following manufacturer's protocols (Anderson, 1998).

Temperature, pH, specific conductance, and nephelometric turbidity of the purge water from each well were measured to ensure stabilization before sample collection. Well purging was considered complete when values stabilized to within 1°C for temperature, 0.25 standard units for pH, 50  $\mu\text{S}/\text{cm}$  for specific conductance, and within 10 percent for turbidity.

Samples were collected, filtered, and stored in accordance with USEPA and USGS (U.S. Geological Survey, variously dated) procedures, depending on the laboratory providing analyses. Samples for boron and boron isotope analysis used to evaluate the sources of boron in ground water were not acidified. Four water samples collected in November 2004 for boron analysis were acidified to compare with the results of unacidified samples.



**Figure 9.** Well 9A with the Yard 520 landfill in the background, facing southwest at the Town of Pines, Indiana (Photograph by Paul M. Buszka, U.S. Geological Survey, July 31, 2007).



(A)



(B)

**Figure 10.** (A) View facing west of well 5W in the surficial aquifer at a National Park Service public facility, and (B) view facing southwest of homes that are upgradient of well 5W along the Lake Michigan shore at Beverly Shores, Indiana (Photograph by Lee R. Watson, U.S. Geological Survey, March 28, 2005).



**Figure 11.** An example of a suspected domestic-wastewater seep at Beverly Shores, Indiana (Photograph by Lee R. Watson, U.S. Geological Survey, March 28, 2005).

Two test mixtures were prepared with deionized water and a borax detergent additive (one sample) and a detergent with a sodium perborate bleach (one sample); the additive and detergent were purchased from a local supermarket. One sample of each mixture was prepared to identify similarities to the domestic-wastewater-affected samples.

### Laboratory Analyses of Water Samples

Water samples collected during this investigation were sent to several laboratories for analysis (table 3). Water samples were analyzed for concentrations of boron (26 samples), chloride (24 samples), sulfate (24 samples), ammonia as nitrogen (26 samples), nitrite plus nitrate as nitrogen (26 samples), and strontium (26 samples). Water samples also were analyzed for the stable isotope ratios  $\delta^{11}\text{B}$  (boron-11/boron-10) (26 samples) and  $\delta^{18}\text{O}$  (oxygen-18/oxygen-16) (10 samples), for ratios of the decaying isotope strontium-87 to the stable isotope strontium-86 (strontium-87/strontium-86)

(26 samples), and for concentrations of the decaying isotope, tritium (hydrogen-3; 18 samples).

Analyses of boron isotope ratios were done at the USGS National Research Program laboratory in Menlo Park, California with methods consistent with those reported by Bayless and others (2004). For purposes of this investigation, boron isotopes were reported as  $\delta^{11}\text{B}$ , in per mil or the deviation of the  $^{11}\text{B}/^{10}\text{B}$  ratio of the sample from that of a standard boric acid sample, NIST-951, as described by Davidson and Bassett (1993).

$$\delta^{11}\text{B} = \left\{ \left[ \frac{(^{11}\text{B}/^{10}\text{B})_{\text{sample}} - (^{11}\text{B}/^{10}\text{B})_{\text{standard}}}{(^{11}\text{B}/^{10}\text{B})_{\text{standard}}} \right] \right\} * 1000 \quad (1)$$

The ratios of boron (B) isotopes were measured with a multicollector thermal-ionization mass spectrometer in negative-ion mode (NTIMS) (Finnigan MAT 261). An amount of water or sample sufficient to provide approximately 2 nanograms of boron was loaded directly onto rhenium filaments. The ideal load volume of water sample onto the filament was 1-20 microliters. If the concentration of the sample was not

sufficient to allow this small sample size, then the sample was pre-concentrated by partial evaporation in a Teflon beaker. Rhenium filaments were then outgassed under  $10^{-2}$  Pa at 1.4 amperes of filament current for 1 to 2 minutes to dry the sample onto the filament. The filaments were loaded immediately into the NTIMS and placed under vacuum in preparation for analysis.

Measurements of boron isotopes were made at an operating voltage of 10 kilovolts by the NTIMS. The collector measuring resistor was  $10^{11}$  ohms. The ionic species detected by the NTIMS for boron isotope ratios were  $\text{BO}_2^-$  at 42 and 43 amu that serve as direct proxies for  $^{10}\text{B}$  and  $^{11}\text{B}$ , respectively. The ion-beam intensity to record a signal at 43 amu ranged from 1 to 4 volts by adjusting the filament current and by focusing the lens assemblies in the source to maximize the signal intensity. The filament currents varied from about 1.4 to 1.6 amperes. The typical temperatures of operation were 900 to 1,000°C. A boron isotope ratio was collected for 8 seconds, and 10 ratios were collected in each block of measurements. Baseline measurements were made at 42.5 amu before data collection for each block. Signal intensity for each isotope was corrected accordingly.

A boric acid isotope standard (NIST-951) and sea water were measured daily during the analyses; samples were analyzed when the reported B isotope ratio for sea water in relation to NIST-951 was within the long-term (5-year) 2-sigma range of replicate values ( $\delta^{11}\text{B} = +39.2 \pm 0.5$  per mil). All samples were analyzed at least twice to assure reasonable reproducibility, ideally within 1 per mil.

Ratios of strontium isotopes were measured in water samples using methods consistent with those reported in Bayless and others (2004). Strontium isotopes were reported as a concentration ratio of strontium-87 to strontium-86. Strontium isotope analyses were done on a Finnigan MAT 261 multicollector thermal-ionization mass spectrometer in positive-ion mode (PTIMS). The strontium was separated and purified, using cation exchange chromatography in a clean laboratory with Teflon-distilled reagents. The purified samples were loaded on tantalum filaments and the isotope ratios were measured, using PTIMS. A strontium standard reference material, NIST-987, was analyzed daily; water samples were analyzed only if the isotope ratio for the standard reference material was within the long-term (5-year) 2-sigma range of replicate values (strontium-87/strontium-86 = 0.71024  $\pm$  0.00002).

Selected samples were analyzed for concentrations of tritium by the USGS National Research Program laboratory

in Menlo Park, California (table 3). Tritium is a radioactive isotope of hydrogen with an atomic mass of 3 and a half-life of 12.3 years (Lucas and Unterweger, 2000). A typical hydrogen atom (hydrogen-1) has one proton in the nucleus; the nucleus of tritium has one proton and two neutrons. Tritium decays to a daughter compound, helium-3, by emitting a beta particle (an electron) through decay of one of the neutrons. Tritium concentrations were analyzed by counting the rate of beta (electron) emissions from neutron decay and are expressed in tritium units. For comparison to other work, 3.2 picocuries of tritium per liter is equal to 1 tritium unit (TU). A tritium unit is equal to 1 tritium atom for every  $10^{18}$  atoms of hydrogen. For 1 L of water, 1 TU is equivalent to 0.12 disintegrations of a tritium atom per second.

Estimates of ground-water age were made, using the activity of tritium in water in comparison to its activity in precipitation and other potential contributing sources. Tritium is produced naturally by the bombardment of nitrogen in the atmosphere by cosmic radiation (Grosse and others, 1951) and is added to the atmosphere from the solar wind. Atmospheric tritium and oxygen then combine to form water, which enters the ground-water system through infiltration of precipitation. Although few measurements are available, it is estimated that the natural concentration of tritium in precipitation is between 5 and 20 TU (Kauffman and Libby, 1954).

Synthetic tritium was released to the atmosphere in large amounts during the testing of atmospheric thermonuclear devices between 1952 and 1980, with the greatest inputs from 1952 through 1962 (Clark and Fritz, 1997). Tritium concentrations in precipitation were measured monthly since 1953 in samples from a site at Ottawa, Canada, and from January 1962 through December 1979 in samples from a site at Midway Airport in Chicago (fig. 12). Tritium concentrations at Ottawa varied on a monthly basis but increased from about 20 TU in August 1953 to about 5,800 TU in June 1963; since then they have decreased (International Atomic Energy Agency, 2006). The trend of tritium concentrations at Midway Airport was similar to the Ottawa data; they were largest in May 1963 data (3,755 TU) and gradually decreased to 21.1 TU by November 1979. The trends in the more-complete record of Ottawa data are used in this investigation to interpret tritium concentrations in precipitation. By about 1990, synthetic tritium had been largely removed from the atmosphere and tritium concentrations in precipitation had returned to near natural levels.

**Table 3.** Analytical methods for ground-water samples collected near Beverly Shores, Indiana, 2004.

[–, not available or not known; USGS, U.S. Geological Survey; NFM, National Field Manual;  $\mu\text{S}/\text{cm}$ , microsiemen per centimeter;  $^{\circ}\text{C}$ , degree Celsius;  $\text{mg}/\text{L}$ , milligram per liter; USEPA, U.S. Environmental Protection Agency; IC, ion chromatography; N, nitrogen; ASF, automated-segmented flow;  $\mu\text{g}/\text{L}$ , microgram per liter; ICP, inductively-coupled plasma; MS, mass spectroscopy; TU, tritium unit]

Constituent or property name	Chemical abstracts service identification number	Reporting unit	Source of analysis	Analytical method description
Properties				
Turbidity	–	Nephelometric turbidity unit	Field analysis, USGS-NFM Chapter 6.7	Nephelometric turbidimeter, field measurement
pH, field	–	Standard units	Field analysis, USGS-NFM, Chapter 6.4	Multiparameter meter, field measurement
Specific conductance	–	$\mu\text{S}/\text{cm}$	Field analysis, USGS-NFM, Chapter 6.3	Multiparameter meter, field measurement
Temperature	–	$^{\circ}\text{C}$	Field analysis, USGS-NFM, Chapter 6.1	Multiparameter meter, field measurement
Major anions				
Chloride, unfiltered	16887-00-6	$\text{mg}/\text{L}$	USEPA Region 5 Central Regional Laboratory	IC
Sulfate, unfiltered	14808-79-8	$\text{mg}/\text{L}$	USEPA Region 5 Central Regional Laboratory	IC
Nutrients				
Nitrogen, ammonia, unfiltered	7664-41-7	$\text{mg}/\text{L}$ as N	USEPA Region 5 Central Regional Laboratory (USEPA 350.1 NS)	Colorimetry, ASF
Nitrogen, nitrite plus nitrate, unfiltered	–	$\text{mg}/\text{L}$ as N	USEPA Region 5 Central Regional Laboratory (USEPA 353.2)	Colorimetry, ASF, cadmium reduction-diazotization
Trace elements				
Boron, filtered	7440-42-8	$\mu\text{g}/\text{L}$	USGS National Research Program, Isotope Tracers Project laboratory, Menlo Park, California <sup>1</sup>	ICP-MS
Strontium, filtered	7440-24-6	$\mu\text{g}/\text{L}$	USGS National Research Program, Isotope Tracers Project laboratory, Menlo Park, California <sup>1</sup>	ICP-MS



**Table 3.** Analytical methods for ground-water samples collected near Beverly Shores, Indiana, 2004.—Continued

[—, not available or not known; USGS, U.S. Geological Survey; NFM, National Field Manual;  $\mu\text{S}/\text{cm}$ , microsiemen per centimeter;  $^{\circ}\text{C}$ , degree Celsius;  $\text{mg}/\text{L}$ , milligram per liter; USEPA, U.S. Environmental Protection Agency; IC, ion chromatography; N, nitrogen; ASF, automated-segmented flow;  $\mu\text{g}/\text{L}$ , microgram per liter; ICP, inductively-coupled plasma; MS, mass spectroscopy; TU, tritium unit]

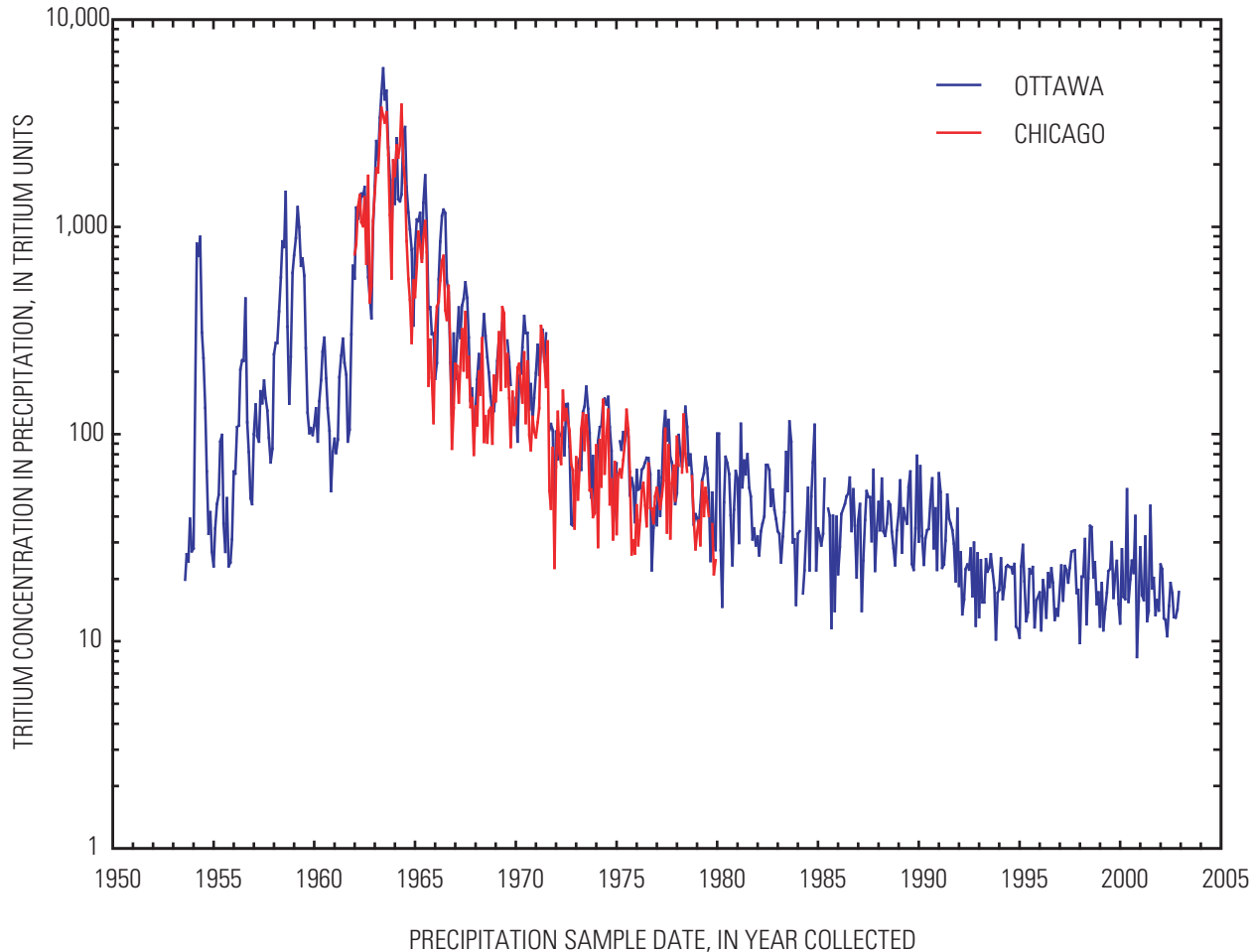
Constituent or property name	Chemical abstracts service identification number	Reporting unit	Source of analysis	Analytical method description
Isotopes				
Tritium, unfiltered	10028-17-8	TU	USGS National Research Program project laboratory, Menlo Park, California	Isotope ratio-MS
Boron-11/boron-10, filtered, reported as $\delta^{11}\text{B}$	—	per mil <sup>2</sup>	USGS National Research Program, Isotope Tracers Project laboratory, Menlo Park, California	Multicollector thermal-ionization MS, negative-ion mode
Strontium-87/strontium-86 ratio, filtered	—	Molar ratio	USGS National Research Program, Isotope Tracers Project laboratory, Menlo Park, California	Multicollector thermal-ionization MS, positive-ion mode
Oxygen-18/oxygen-16, unfiltered, reported as $\delta^{18}\text{O}$	—	per mil <sup>2</sup>	Northern Illinois University, Department of Geology and Environmental Geosciences, DeKalb, Illinois	Isotope ratio-MS

<sup>1</sup>Garbarino (1999)

<sup>2</sup>Boron ( $\delta^{11}\text{B}$ ) and oxygen ( $\delta^{18}\text{O}$ ) isotope data were reported in per mil or the deviation of the  $^{11}\text{B}/^{10}\text{B}$  and  $^{18}\text{O}/^{16}\text{O}$  ratio of the sample from that of a standard material, using the following formulas:

$\delta^{11}\text{B} = \{[(^{11}\text{B}/^{10}\text{B}) \text{ sample} - (^{11}\text{B}/^{10}\text{B}) \text{ standard}] / (^{11}\text{B}/^{10}\text{B}) \text{ standard}\} * 1000$ , where the standard is a boric acid sample, NIST-951 (Davidson and Bassett, 1993)

$\delta^{18}\text{O} = \{[(^{18}\text{O}/^{16}\text{O}) \text{ sample} - (^{18}\text{O}/^{16}\text{O}) \text{ standard}] / (^{18}\text{O}/^{16}\text{O}) \text{ standard}\} * 1000$ , where the standard is Vienna Standard Mean Ocean Water (Clark and Fritz, 1997)



**Figure 12.** The average monthly tritium concentration in precipitation in samples collected from Ottawa, Canada, 1953–2002, and from Chicago, Illinois, 1962–1979 (International Atomic Energy Agency, 2006).

## Evaluation of Ground-Water and Boron Sources

Boron concentrations, boron stable isotope ratios, tritium concentrations, and the other available water-chemistry data (tables 4 and 5) were compared to the results of quality-assurance analyses (tables 6 and 7) and to known potential sources of boron and tritium in representative ground-water samples. Concentrations of boron and other constituents were also compared with applicable Federal water-quality standards as published by the USEPA (2006b, 2006c). The results of the chemical analyses of representative sources of boron in ground water were compared with analyses of ground-water samples from wells with an unknown ground-water source to infer the likely source of the ground water and the associated boron concentrations to the well.

## Quality-Assurance Results

Field quality assurance included multiparameter water-quality-meter calibration, turbidimeter-operation checks, equipment cleaning between sampling sites, sample-custody documentation, and field quality-control samples. Quality-assurance data were collected to identify problems with cleaning of sampling equipment (equipment blanks) and to evaluate the reproducibility of the sampling and analytical techniques (sequential duplicates).

One equipment blank (table 6) was collected during sampling in March 2004. The equipment blank and a sample of deionized water were analyzed for boron and strontium to determine whether samples were being contaminated by the sampling equipment or by residue from previous samples. The equipment blank was prepared by pumping deionized water (obtained from the USEPA) through the sampling apparatus after the pre-sampling cleaning process. Results of this analysis determined that boron concentrations were about equal in the deionized water (20  $\mu\text{g/L}$ ) and the equipment

**Table 4.** Determinations of field parameters for water samples collected from wells near Beverly Shores and the Town of Pines, northwestern Indiana, 2004.

[USGS, U.S. Geological Survey; hhmm, hours and minutes; °C, degree, Celsius; pH, negative logarithm of hydrogen-ion concentration; µS/cm, microsiemen per centimeter; NTU, nephelometric turbidity unit; SA, surficial aquifer; —, no data or not measured]

Project well identifier (figure 2)	USGS station identification number	Date sampled (month/day/year)	Time sampled (hhmm)	Barometric pressure on morning of sampling (millimeters of mercury)	Temperature (°C)	pH (standard units)	Specific conductance (µS/cm)	Turbidity (NTU <sup>1</sup> )
Surficial aquifer wells distant from human-affected boron sources (Surficial-aquifer water)								
1S	414029087003204	03/15/2004	1600	755	7.0	6.9	718	1
2S	413957087002603	03/17/2004	1200	745	5.4	6.2	556	1
3S	414057087003003	03/17/2004	1600	745	9.3	7.4	449	2
4S	414036086590601	03/17/2004	1730	745	4.6	6.85	417	1
Basal sand aquifer wells representing natural boron sources (Basal sand aquifer water)								
1B	414029087003201	03/15/2004	1510	755	11.5	7.80	1,130	2
2B	413957087002601	03/17/2004	1130	745	12.2	7.45	892	31
3B	414057087003000	03/17/2004	1520	745	11.6	7.75	2,050	2
5B	414111086594501	03/18/2004	1000	745	11.5	7.45	1,980	3
		05/26/2004	1230	735	13.2	7.45	1,990	2
Coal-combustion product-affected wells in the surficial aquifer (CCP-affected SA water)								
8A	414050086573001	03/16/2004	0945	747	11.0	6.85	1,810	1
9A	414045086573601	03/16/2004	1050	747	11.7	7.05	1,570	4
10A	414037086572901	03/16/2004	1150	747	7.2	6.95	2,250	153
11A	414046086572301	03/16/2004	1310	747	7.5	6.70	2,010	124
Domestic-wastewater-affected wells in the surficial aquifer (Domestic-wastewater-affected SA water)								
5W	414111086594502	04/19/2004	1230	740	15.0	7.05	620	91
		05/26/2004	1300	735	13.4	7.05	643	2
6W	414101086592001	04/19/2004	1600	740	12.6	6.60	300	11
7W	414108086591801	04/19/2004	1645	740	12.1	6.35	816	9
Wells with an unknown ground-water source								
12U	413953086581801	04/19/2004	1400	740	12.4	7.40	704	2
13U	414052086593201	04/19/2004	1445	740	9.9	6.45	465	1
14U	414048086594201	04/19/2004	1530	740	10.2	7.70	780	6
15U	414050086594001	04/19/2004	1730	—	—	—	—	—
16U	414143086574901	04/19/2004	1745	740	10.7	6.20	166	1
17U	414002086581301	11/17/2004	1145	747	11.9	7.80	613	1
18U	414106086594701	11/17/2004	1500	747	12.2	6.75	2,240	1
19U	414102086595001	11/17/2004	1630	747	15.4	6.35	390	0
20U	414103086594501	11/17/2004	1700	747	14.2	7.85	1,240	2

<sup>1</sup>Turbidity measurements were made, using a Hach Model 2100P nephelometric turbidimeter, serial number 980700018837.



**Table 5.** Water-chemistry determinations for samples collected from wells near Beverly Shores and the Town of Pines, northwestern Indiana, 2004.—Continued

[USGS, U.S. Geological Survey; h:mm, hours and minutes; mg/L, milligram per liter; N, as nitrogen; µg/L, microgram per liter; <, less than; —, no data or not measured; Q, estimated concentration; SA, surficial aquifer; B, boron; TU, tritium unit; O, oxygen; concentrations reported as unfiltered constituents except as noted]

Project well identifier (figure 2)	USGS station identification number	Date sampled (month/day/year)	Time sampled (h:mm)	Isotopes				
				δ <sup>11</sup> B, filtered (per mil <sup>1</sup> )	Strontium-87/strontium-86 ratio, filtered	Tritium (TU)	Tritium, 2-sigma precision (TU)	δ <sup>18</sup> O (per mil <sup>1</sup> )
Surficial aquifer wells distant from human-affected boron sources (Surficial-aquifer water)								
1S	414029087003204	03/15/2004	1600	26.0	0.70941	—	—	-8.39
2S	413957087002603	03/17/2004	1200	24.0	.70968	7.0	0.8	-8.82
3S	414057087003003	03/17/2004	1600	11.2	.70972	8.3	.8	-8.6
4S	414036086590601	03/17/2004	1730	22.1	.70896	8.8	.6	—
Basal sand aquifer wells representing natural boron sources (Basal sand aquifer water)								
1B	414029087003201	03/15/2004	1510	34.0	.70897	—	—	-9.38
2B	413957087002601	03/17/2004	1130	24.6	.70897	<.8	.6	-8.57
3B	414057087003000	03/17/2004	1520	30.1	.70889	<.8	.6	-10.13
5B	414111086594501	03/18/2004	1000	27.9	.70871	—	—	-9.78
		05/26/2004	1230	27.2	.70875	<.8	.6	-9.80
Coal-combustion product affected wells in the surficial aquifer (CCP-affected SA water)								
8A	414050086573001	03/16/2004	0945	0.3	.71169	—	—	—
9A	414045086573601	03/16/2004	1050	3.8	.71104	—	—	—
10A	414037086572901	03/16/2004	1150	0.1	.71091	—	—	—
11A	414046086572301	03/16/2004	1310	6.6	.71100	—	—	—
Domestic-wastewater-affected wells in the surficial aquifer (Domestic-wastewater-affected SA water)								
5W	414111086594502	04/19/2004	1230	11.7	.70960	—	—	-7.78
6W	414101086592001	05/26/2004	1300	9.0	.70957	10.3	.8	-7.84
7W	414108086591801	04/19/2004	1600	10.1	.71095	7.6	.6	—
		04/19/2004	1645	8.7	.71056	8.3	.6	—
Wells with an unknown ground-water source								
12U	413953086581801	04/19/2004	1400	23.8	.70895	<.8	.6	—
13U	414052086593201	04/19/2004	1445	3.6	.71019	7.7	.6	—
14U	414048086594201	04/19/2004	1530	34.1	.70913	<.8	.6	—
15U	414050086594001	04/19/2004	1730	24.9	.70880	<.8	.6	—
16U	414143086574901	04/19/2004	1745	6.6	.70990	8.4	.6	—
17U	414002086581301	11/17/2004	1145	34.7	.70893	<.8	.2	—
18U	414106086594701	11/17/2004	1500	29.2	.70872	<.8	.2	—

**Table 5.** Water-chemistry determinations for samples collected from wells near Beverly Shores and the Town of Pines, northwestern Indiana, 2004.—Continued

[USGS, U.S. Geological Survey; h:mm, hours and minutes; mg/L, milligram per liter; N, as nitrogen; µg/L, microgram per liter; <, less than; —, no data or not measured; Q, estimated concentration; SA, surficial aquifer; B, boron; TU, tritium unit; O, oxygen; concentrations reported as unfiltered constituents except as noted]

Project well identifier (figure 2)	USGS station identification number	Date sampled (month/day/year)	Time sampled (h:mm)	Isotopes				
				δ <sup>11</sup> B, filtered (per mil <sup>1</sup> )	Strontium-87/ strontium-86 ratio, filtered	Tritium (TU)	Tritium, 2-sigma precision estimate (TU)	δ <sup>18</sup> O (per mil <sup>1</sup> )
19U	414102086595001	11/17/2004	1630	12.2	.70919	7.4	.6	—
20U	414103086594501	11/17/2004	1700	28.6	.70891	<.8	.2	—

Wells with an unknown ground-water source—Continued

<sup>11</sup>Boron (δ<sup>11</sup>B) and oxygen (δ<sup>18</sup>O) isotope data were reported in per mil or the deviation of the <sup>11</sup>B/<sup>10</sup>B and <sup>18</sup>O/<sup>16</sup>O ratio of the sample from that of a standard material, using the following formulas:

δ<sup>11</sup>B = {[(<sup>11</sup>B/<sup>10</sup>B) sample - (<sup>11</sup>B/<sup>10</sup>B) standard] / (<sup>11</sup>B/<sup>10</sup>B) standard} \* 1000, where the standard is a boric acid sample, NIST-951 (Davidson and Bassett, 1993)

δ<sup>18</sup>O = {[(<sup>18</sup>O/<sup>16</sup>O) sample - (<sup>18</sup>O/<sup>16</sup>O) standard] / (<sup>18</sup>O/<sup>16</sup>O) standard} \* 1000, where the standard is Vienna Standard Mean Ocean Water (Clark and Fritz, 1997)

**Table 6.** Water-chemistry determinations for samples and sequential duplicates collected from wells near Beverly Shores and the Town of Pines, northwestern Indiana, and for deionized water and an equipment blank, 2004.

[USGS, U.S. Geological Survey; mg/L, milligram per liter; N, as nitrogen, µg/L, microgram per liter; –, no data or not measured; RPD, relative percent difference; <, less than; >, greater than; Q, estimated concentration; NC, not computed; USEPA, U.S. Environmental Protection Agency; bold value indicates relative percent difference statistic greater than 25 percent; concentrations reported as unfiltered constituents except as noted]

Project well identifier (figure 2)	USGS station identification number	Date sampled (month/day/year)	Sample type	Major ions, nutrients, and boron				
				Chloride (mg/L)	Sulfate (mg/L)	Ammonia (mg/L as N)	Nitrite plus nitrate (mg/L as N)	Boron, filtered unacidified (µg/L)
1S	414029087003204	03/15/2004	Sample	–	–	–	–	688
			Sequential duplicate	–	–	–	–	626
			RPD, in percent <sup>1</sup>					9.4
1B	414029087003201	03/15/2004	Sample	–	–	–	–	1,750
			Sequential duplicate	–	–	–	–	1,800
			RPD, in percent					2.4
5B	414111086594501	03/18/2004	Sample	443	47.8	0.81	< 0.03	1,534
			Sequential duplicate	858	46.5	.84	15.6	1,437
			RPD, in percent	<b>64</b>	2.8	3.6	<b>&gt;199</b>	6.5
6W	414101086592001	04/19/2004	Sample	–	–	–	–	98
			Sequential duplicate	–	–	–	–	107
			RPD, in percent					8.8
8A	414050086573001	03/16/2004	Sample	25.2	531	1.85	Q .66	20,600
			Sequential duplicate	25.4	536	1.85	13.6	–
			RPD, in percent	.79	.94	.00	<b>182</b>	NC
9A	414045086573601	03/16/2004	Sample	–	–	–	–	16,200
			Sequential duplicate	–	–	–	–	14,700
			RPD, in percent					9.7
12U	413953086581801	04/19/2004	Sample	–	–	–	–	436
			Sequential duplicate	–	–	–	–	390
			RPD, in percent					11.1
14U	414048086594201	04/19/2004	Sample	–	–	–	–	1,920
			Sequential duplicate	–	–	–	–	1,760
			RPD, in percent					8.3
16U	414143086574901	04/19/2004	Sample	–	–	.57	<.03	Q 37
			Sequential duplicate	–	–	.7	<.03	39
			RPD, in percent	–	–	20.47	NC	5.3
18U	414106086594701	11/17/2004	Sample	579	Q 98.9	Q .72	Q <.03	1,160
			Sequential duplicate	577	Q103	Q .66	Q <.03	–
			RPD, in percent	.35	4.1	8.7	NC	NC

**Table 6.** Water-chemistry determinations for samples and sequential duplicates collected from wells near Beverly Shores and the Town of Pines, northwestern Indiana, and for deionized water and an equipment blank, 2004.—Continued

[USGS, U.S. Geological Survey; mg/L, milligram per liter; N, as nitrogen, µg/L, microgram per liter; –, no data or not measured; RPD, relative percent difference; <, less than; >, greater than; Q, estimated concentration; NC, not computed; USEPA, U.S. Environmental Protection Agency; bold value indicates relative percent difference statistic greater than 25 percent; concentrations reported as unfiltered constituents except as noted]

Project well identifier (figure 2)	USGS station identification number	Date sampled (month/day/year)	Sample type	Trace elements	
				Boron, filtered, unacidified (µg/L)	Strontium, filtered (µg/L)
8A	414050086573001	03/16/2004	USEPA deionized water	20.	41.1
			Equipment blank	19.5	44.9
			RPD, in percent	2.5	8.8

<sup>1</sup>The RPDs were computed for the paired water sample and sequential duplicate as

$$RPD = |(SD-WS)/((SD+WS)/2)| \times 100,$$

Where RPD is the relative percent difference, SD is the concentration in the sequential duplicate or equipment blank, and WS is the concentration in the water sample.

**Table 7.** Comparison of boron determinations from analyses of acidified and unacidified samples from wells near Beverly Shores and the Town of Pines, northwestern Indiana, November 2004.

[USGS, U.S. Geological Survey; µg/L, microgram per liter; B, boron; concentrations reported as filtered constituents]

Project well identifier (figure 2)	USGS station identification number	Boron, unacidified sample (µg/L) <sup>1</sup>	Boron, acidified sequential duplicate (µg/L) <sup>2</sup>	Relative percent difference between unacidified and acidified samples <sup>3</sup>	δ <sup>11</sup> B of unacidified sample (per mil <sup>4</sup> )	Estimated δ <sup>11</sup> B of acidified sample (per mil <sup>4,5</sup> )	Difference between estimated δ <sup>11</sup> B of unacidified sample and δ <sup>11</sup> B of acidified sample (per mil <sup>4</sup> )
17U	414002086581301	1,210	1,420	16.0	28.6	25.8	2.8
18U	414106086594701	1,160	1,330	13.7	29.2	26.8	2.4
19U	414102086595001	126	141	11.2	12.2	10.1	2.0
20U	414103086594501	1,340	1,490	10.7	34.7	32.8	1.9

<sup>1</sup> The water sample was collected, filtered through a 0.45 micrometer capsule filter, and then sent to the USGS Menlo Park, California laboratory for boron and boron isotope analysis.

<sup>2</sup> A sequential duplicate was collected immediately after the water sample, filtered through a 0.45 micrometer capsule filter, acidified by addition of 1 normal sulfuric acid to a pH of less than 2, and analyzed at the USGS National Water Quality Laboratory for analysis.

<sup>3</sup> The relative percent differences were computed for the paired water sample and sequential duplicate as

$$RPD = |(SD-WS)/((SD+WS)/2)| \times 100,$$

where

RPD is the relative percent difference,  
SD is the concentration in the acidified sequential duplicate, and  
WS is the concentration in the unacidified water sample.

<sup>4</sup> Boron (δ<sup>11</sup>B) and oxygen (δ<sup>18</sup>O) isotope data were reported in per mil or the deviation of the <sup>11</sup>B/<sup>10</sup>B and <sup>18</sup>O/<sup>16</sup>O ratio of the sample from that of a standard material, using the following formulas:

$$\delta^{11}\text{B} = \{[(^{11}\text{B}/^{10}\text{B}) \text{ sample} - (^{11}\text{B}/^{10}\text{B}) \text{ standard}] / (^{11}\text{B}/^{10}\text{B}) \text{ standard}\} * 1000, \text{ where the standard is a boric acid sample, NIST-951}$$

<sup>5</sup> The δ<sup>11</sup>B in an acidified sample was estimated, using the following equation that is modified from an equation used by Vengosh and others (1994) to simulate the fractionation of boron isotopes where boron is adsorbed from water by clay minerals:

$$Y = [(Z+1000) - (1000/(\alpha - \alpha X + X))]$$

where

Y is the estimated δ<sup>11</sup>B of an acidified sample,  
Z is the δ<sup>11</sup>B of the unacidified sample,  
α is the fractionation factor between the dissolved and adsorbed boron assumed to be 0.981, Kakhana and others, 1977), and  
X is the fraction of boron remaining in solution after sorption, represented by the boron concentration of the unacidified sample, in micromoles per liter, divided by the boron concentration in the acidified sample, in micromoles per liter.



blank (19.5 µg/L) and that boron was not added to samples by the sampling apparatus and cleaning process. Strontium concentrations were larger in the equipment blank (44.9 µg/L) than in the deionized water (41.1 µg/L); this corresponds to a difference of about 3.8 µg/L between the two samples. The data indicate that very small amounts of strontium may have been added to the equipment blank by the sampling apparatus and cleaning process.

Sequential duplicate samples were collected and analyzed from four wells (5B, 8A, 16U, and 18U) to help verify the reproducibility of the sampling techniques for analyses of chloride, sulfate, ammonia, and nitrite plus nitrate (table 6). In addition, sequential duplicate samples were collected and analyzed from eight wells (1S, 1B, 5B, 6W, 9A, 12U, 14U, and 16U) for boron analyses (table 6). A sequential duplicate is a sample collected in immediate succession to the water sample from the same source, using the same equipment and methods. The difference between analyses from a water sample and its sequential duplicate was evaluated, using the relative percent difference (RPD) statistic. The RPD is the absolute value of the difference of the two concentrations of a single constituent divided by the average of the two concentrations, expressed as a percent (table 6).

RPD values were greater than 25 percent for nitrite plus nitrate data from well 8A on March 16, 2004, and chloride and nitrite plus nitrate data from well 5B on March 18, 2004 (table 6). The nitrite plus nitrate and chloride analyses of these water samples were not reported in table 5 because of the large disagreement between analytical results from the water sample and the sequential duplicate. The RPD values for boron data ranged from 2.4 to 11.1 (table 6). All boron analyses were presented in the data tables without qualification.

Sequential duplicates were not analyzed for boron isotope ratios and tritium concentrations. Two to three replicate boron analyses were made from each sample at the laboratory by extracting the same volume for analysis. The difference in boron isotope ratios ( $^{11}\text{B}/^{10}\text{B}$ ) in 42 replicate analyses varied from 0 (no difference) to 0.021, with an average difference of 0.008. Tritium analyses were done by a liquid scintillation counting technique, using replicate counts on the same volume of water; the data are reported with a 2-sigma precision estimate that ranged from 0.2 to 0.8 TU (table 5).

Samples from four wells were collected for boron analysis during November 2004 (table 5) to evaluate the effect of acid preservation on the analytical results. A sequential duplicate was collected from each well; it was acidified by addition of 1 normal sulfuric acid to a pH of less than 2 and then sent to the USGS National Water Quality Laboratory for analysis. Boron concentrations determined from four acidified sequential duplicates were larger than those measured in unacidified samples (table 7). RPDs ranged from about 10.7 to 16 percent. USGS analyses of boron typically are made on acidified samples to prevent scavenging of trace elements from solution by adsorption onto ferric oxyhydroxide and other precipitates. Boron and  $\delta^{11}\text{B}$  analyses for this investigation were made on unacidified samples to assure consistency of the result with

unacidified analyses of  $\delta^{11}\text{B}$  values from other investigations (Vengosh and others, 1994; Buszka and others, 1994; Davidson and Bassett, 1993; Leenhouts and others, 1998; Verstraeten and others, 2005; Barth, 1998; Oi and others, 1989). The result of this comparison indicated that boron concentrations reported for this investigation may be from about 11 to 16 percent less than would be reported in a standard analysis of an acidified sample.

The loss of boron from unacidified samples may have decreased the  $\delta^{11}\text{B}$  values of those samples, in comparison to acidified samples. Barth (1993) summarized results of other studies that identified fractionation or differential uptake of  $^{11}\text{B}$  in comparison to  $^{10}\text{B}$  in the boron adsorbed by clay minerals and other adsorbents. Boron in natural water principally is present as the uncharged  $\text{B}(\text{OH})_3^0$  species at a pH less than 9.2 and the negatively charged  $\text{B}(\text{OH})_4^-$  at pH values greater than 9.2. During isotope exchange, the lighter isotope  $^{10}\text{B}$  is preferentially partitioned into  $\text{B}(\text{OH})_4^-$  (Kakihana and others, 1977). Water affected by sorption of B would have a larger  $\delta^{11}\text{B}$  value because the charged  $\text{B}(\text{OH})_4^-$  is adsorbed more strongly by clay minerals than is the neutral  $\text{B}(\text{OH})_3^0$ .

The potential effect of sorption-related fractionation of boron on unacidified samples was evaluated by computing the  $\delta^{11}\text{B}$  value that would have resulted from the measured loss of B from solution in samples 17U through 20U (table 7). These samples, although from wells with an unknown ground-water source, are within the range of constituent concentrations and property values in all potential sources except the CCP-affected SA water (table 5). The field pH of these samples ranged from 6.35 to 7.85 (table 4); the amount of boron typically present in solution as  $\text{B}(\text{OH})_4^-$  ranges from near zero at a pH of 7 to about 20 percent at a pH near 8 (Palmer and others, 1987, p. 2,321). The  $\delta^{11}\text{B}$  in an acidified sample was estimated, using the following equation that is modified from an equation used by Vengosh and others (1994) to simulate the fractionation of boron isotopes where boron is adsorbed from water:

$$Y = [(Z + 1000) - 1000 / (\alpha - \alpha X + X)] \quad (2)$$

where

- $Y$  is the estimated  $\delta^{11}\text{B}$  of an acidified sample
- $Z$  is the  $\delta^{11}\text{B}$  of the unacidified sample
- $\alpha$  is the fractionation factor between the dissolved and adsorbed boron (assumed to be 0.981 from column-adsorption experiments, Kakihana and others, 1977), and
- $X$  is the fraction of boron remaining in solution after sorption, represented by the boron concentration of the unacidified sample, in micromoles per liter, divided by the boron concentration in the acidified sample, in micromoles per liter.

This computation uses a column-experiment-based fractionation factor ( $\alpha$ ) that describes sorption of boron as a

substitute for one based on sorption by amorphous ferric oxyhydroxide minerals. Amorphous ferric oxyhydroxide minerals are likely the principal precipitate from the water samples, based on the slight orange tint in several samples. No isotope fractionation factors for boron adsorption onto amorphous ferric oxyhydroxide minerals were available in the literature.

The  $\delta^{11}\text{B}$  values estimated for acidified samples were depleted by 1.9 to 2.8 per mil, in comparison to unacidified samples from the four wells sampled (table 7). The differences in  $\delta^{11}\text{B}$  values between acidified and unacidified samples were small, in comparison to the differences between  $\delta^{11}\text{B}$  values of representative ground-water sources of boron (table 5). By comparison, if boron losses were from incorporation of boron into the amorphous precipitate, fractionation-related changes in  $\delta^{11}\text{B}$  values would be less than those in the adsorption-based estimate. Incorporation-based losses of boron would include  $\text{B}(\text{OH})_3^0$  and  $\text{B}(\text{OH})_4^-$ , thereby minimizing any changes based on preferential sorption or inclusion of  $\text{B}(\text{OH})_4^-$  in comparison to  $\text{B}(\text{OH})_3^0$ . Based on this comparison among four water samples, it is reasonable to assume that the loss of boron through adsorption from unacidified samples did not produce changes that would prevent the use of  $\delta^{11}\text{B}$  data from unacidified samples to identify differences among the samples of representative ground-water sources of boron.

## Boron and Boron Stable-Isotopes in Representative Ground-Water Sources

Boron concentrations were largest in samples of CCP-affected SA water from wells (8A, 9A, 10A and 11A) at the Yard 520 landfill (15,700 to 24,400  $\mu\text{g/L}$ ) and smallest in three of four wells (2S, 3S, and 4S) in the surficial aquifer that were distant from human-affected boron sources (27 to 63  $\mu\text{g/L}$ ) (table 5). Boron concentrations in water from the basal sand aquifer ranged from 656  $\mu\text{g/L}$  in a sample from well 2B to 1,800  $\mu\text{g/L}$  in a sample from well 3B. By comparison, the median boron concentration in 14 acid-preserved ground-water samples collected in 1980 from the basal sand aquifer was 730  $\mu\text{g/L}$  (Shedlock and others, 1994, table 6, p. 42). Boron concentrations in water from three domestic-wastewater-affected SA wells (5W, 6W and 7W) ranged from 84 to 387  $\mu\text{g/L}$ . Among the representative ground-water sources, boron concentrations in water from all four samples of CCP-affected SA water and four of five samples of water from the basal sand aquifer had concentrations greater than the USEPA RAL of 900  $\mu\text{g/L}$  for drinking water (table 5).

It was possible to chemically distinguish among CCP-affected SA water, domestic-wastewater-affected SA water, and water from the basal sand aquifer by comparing boron concentrations with boron isotope ratios in ground-water samples representative of potential boron sources (fig. 13). The largest boron isotope ratios, ranging from 24.6 to 34.0 per mil were in water from the basal sand aquifer (table 5). The smallest boron isotope ratios among representative ground-water sources, ranging from 0.1 to 6.6 per mil were in CCP-affected SA water

(table 5). Boron isotope ratios in domestic-wastewater-affected SA water that ranged from 8.7 to 11.7 per mil; these values were between those of CCP-affected SA water and basal sand aquifer water. Boron isotope ratios in analyses of prepared samples of a borax detergent additive and a detergent with sodium perborate bleach were similar to or less than those of CCP-affected SA water (table 8).

Boron isotope ratios for CCP-affected SA water from wells at the Yard 520 landfill generally were enriched in boron-11, in comparison to the small amount of published data for CCP-affected leachates (table 9). Davidson and Bassett (1993) reported values of  $\delta^{11}\text{B}$  for four samples of laboratory-prepared CCP (fly ash) leachate of 15.8, -19.2, -4.1, and -7.9 per mil. Spivack-Birndorf and Stewart (2006) reported  $\delta^{11}\text{B}$  values ranging from -17 to -16 per mil for two water samples prepared in a laboratory by ultrapure water leaching of two different samples of CCP (fly ash) and -13 per mil for a similar leaching of one sample of flue-gas desulfurization gypsum. Data reported here and published data support the interpretation by Davidson and Bassett (1993) that the  $\delta^{11}\text{B}$  values of CCP-affected SA water are variable and specifically should be determined for each investigation when used to indicate a CCP-related contaminant source.

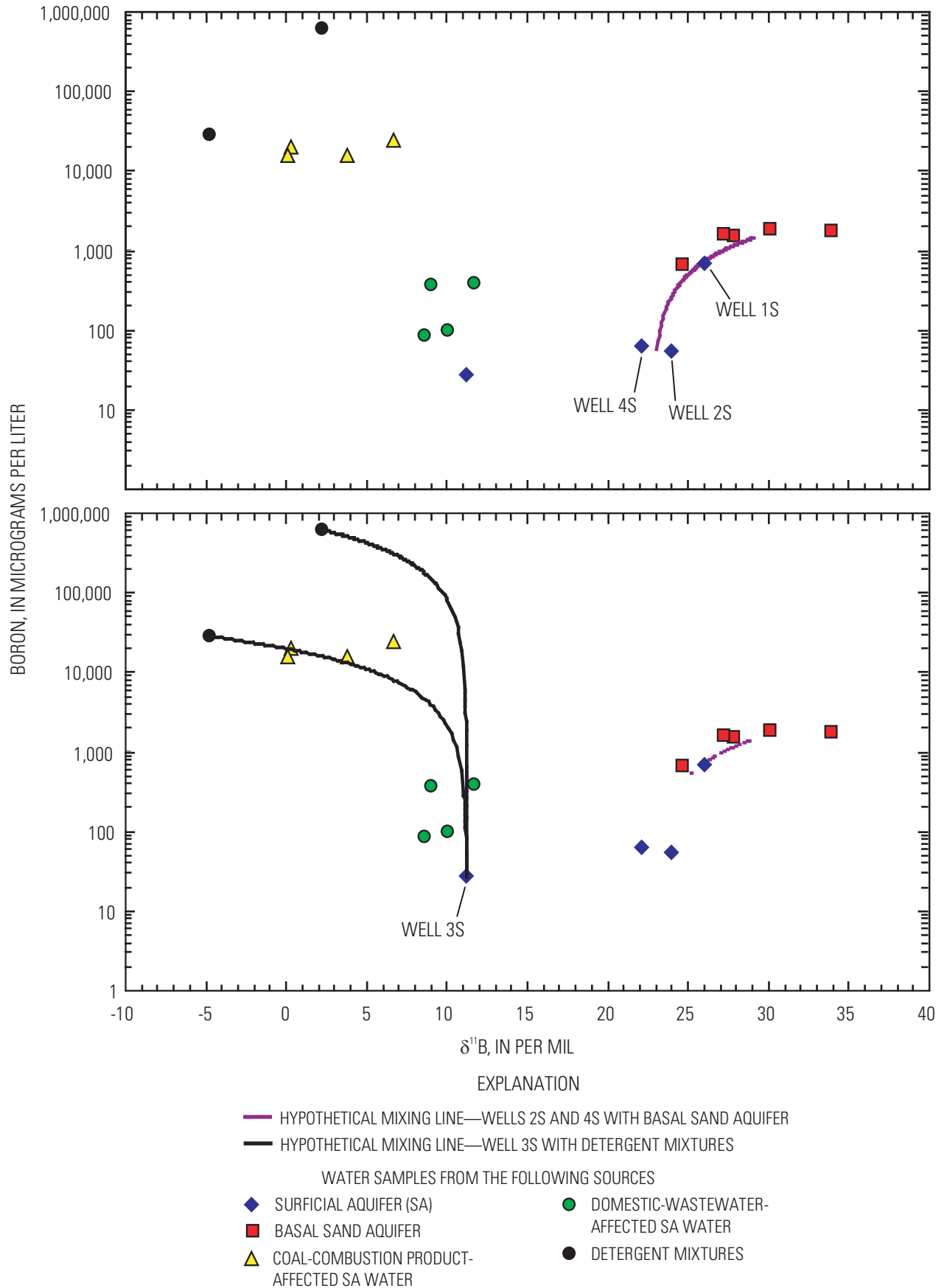
Boron concentrations and boron isotope ratios in two water samples from the surficial aquifer that were distant from human-affected boron sources were similar to those in other representative ground-water sources. The boron concentration and boron isotope ratio in the sample from well 1S were similar to those in water from the basal sand aquifer. Boron isotope ratios in samples from wells 2S and 4S were similar to those in water from the basal sand aquifer; boron concentrations in those samples were about 10 to 12 times less than the smallest boron concentration from the basal sand aquifer (table 5, fig. 13).

Assuming that the water samples from wells 2S and 4S are representative of surficial-aquifer water with naturally small boron concentrations, a hypothetical mixing line was computed using the following equation and drawn for (1) a mixture of equal parts of water from wells 2S and 4S with (2) an average composition of representative ground-water samples from the basal sand aquifer (fig. 13). Concentrations of boron or ratios of boron stable isotopes in hypothetical mixtures were computed using the formula

$$A(\text{mixture}) = F(\text{sa}) \times A(\text{sa}) + F(\text{bsa}) \times A(\text{bsa}) \quad (3)$$

where:

- $A$  is the concentration of boron or a  $^{11}\text{B}/^{10}\text{B}$  ratio
- $F$  is the fractional volume of an representative composition in a hypothetical mixture
- $\text{sa}$  indicates a characteristic representing a mixture of equal parts of water from wells 2S and 4S in the surficial aquifer
- $\text{bsa}$  indicates an average composition of representative ground-water samples from the basal sand aquifer.



**Figure 13.** Chemistry of water samples from wells in and near Beverly Shores, northwestern Indiana, 2004, in relation to boron isotope composition and boron concentrations for representative sources of boron in ground water.

**Table 8.** Boron and boron stable-isotope analyses of a borax detergent additive and a detergent with perborate bleach, 2004.

[µg/L; microgram per liter; B, boron; mL, milliliters]

Detergent characteristic	Details of sample preparation	Boron, unacidified sample (µg/L)	δ <sup>11</sup> B (per mil <sup>1</sup> )
Borax detergent additive	0.1 gram of additive dissolved in 20 mL of deionized water	603,000	2.3
Detergent with perborate bleach	1 gram of detergent dissolved in 100 mL of deionized water	28,100	-4.8

<sup>1</sup>Boron (δ<sup>11</sup>B) isotope data were reported in units of per mil, or the deviation of the <sup>11</sup>B/<sup>10</sup>B ratio of the sample from that of a standard material, using the following formula:

$$\delta^{11}\text{B} = \{[(^{11}\text{B}/^{10}\text{B}) \text{ sample} - (^{11}\text{B}/^{10}\text{B}) \text{ standard}] / (^{11}\text{B}/^{10}\text{B}) \text{ standard}\} * 1000,$$

where the standard is a boric acid sample, NIST-951

**Table 9.** Ranges of boron isotope ratios in samples of representative ground-water sources of boron collected in the study area near Beverly Shores, northwestern Indiana, 2004 and of detergent additive and detergent samples, 2004, as compared to selected published data.

[B, boron; –, no value available]

Potential boron source	Range of δ <sup>11</sup> B, this investigation (per mil <sup>1</sup> )	Ranges of δ <sup>11</sup> B, published values (per mil <sup>1</sup> )
Coal-combustion product affected water	0.1 to 6.6, four samples from four wells in the surficial aquifer	Laboratory-prepared leachate samples, by material -17 to -16, two fly-ash samples, bituminous coal (1) 15.8, fly ash, sub-bituminous coal, front-fire furnace combustion, one sample (2) -19.2, fly ash, bituminous coal, front-fired furnace combustion, one sample (2) -4.1, fly ash, bituminous coal, cyclone-furnace combustion, one sample (2) -7.9, fly ash, lignite, tangential-furnace combustion, one sample (2) -13, flue-gas desulfurization, one sample (1)
Domestic-wastewater-affected surficial-aquifer water	8.7 to 11.7, four samples from three wells in the surficial aquifer	6.0 to 10.6, treated wastewater, four samples, Texas (3) 7.6 to 12.9, raw sewage, three samples, Israel (4) 5.3 to 11.0, treated sewage, three samples, Israel (4) -2.7, treatment-plant effluent, one sample, Nevada (5) 2.2, treatment-plant effluent, one sample, Arizona (6) -0.2 and 0.7 per mil, two samples suspected to be affected by septic waste, Nebraska (7) -5.7, wash water from a domestic washing machine, one sample, Nevada (5)
Borax detergent additive	2.3, one sample	-4.76 to 0.91, sodium perborate and sodium tetraborate, eight samples (8)
Detergent with perborate bleach	-4.3, one sample	–
Sodium borate minerals	–	-0.9 to 10.2, borax, four samples; tincal, four samples; kernite, one sample, California (9)

<sup>1</sup>Boron (δ<sup>11</sup>B) isotope data were reported in per mil or the deviation of the <sup>11</sup>B/<sup>10</sup>B ratio of the sample from that of a standard material, using the following formula:

$$\delta^{11}\text{B} = \{[(^{11}\text{B}/^{10}\text{B}) \text{ sample} - (^{11}\text{B}/^{10}\text{B}) \text{ standard}] / (^{11}\text{B}/^{10}\text{B}) \text{ standard}\} * 1000, \text{ where the standard is a boric acid sample, NIST-951}$$

References: (1) Spivack-Birndorf and Stewart (2006), (2) Davidson and Bassett (1993), (3) Buszka and others (1994) and Bassett and others (1995), (4) Vengosh and others (1994), (5) Seiler (2005), (6) Leenhouts and others (1998), (7) Verstraeten and others (2005), (8) Barth (1998), (9) Oi and others (1989)

The  $^{11}\text{B}/^{10}\text{B}$  of the hypothetical mixture then was converted to  $\delta^{11}\text{B}$  values, in per mil, or the deviation of the  $^{11}\text{B}/^{10}\text{B}$  ratio of the sample from that of a standard material, using the formula in equation (1). Water from well 1S plots along this hypothetical mixing line (fig. 13). The boron content of the sample from well 1S in the surficial aquifer therefore likely was affected by long-term, upward discharge of boron-enriched water from the basal sand aquifer through the till and lacustrine clay and silt confining unit.

$\delta^{11}\text{B}$  values in domestic-wastewater-affected SA water samples were similar to values previously reported for treated and untreated wastewater (table 9) (Buszka and others, 1994; Bassett and others, 1995; Vengosh and others, 1994).  $\delta^{11}\text{B}$  values in domestic-wastewater-affected SA water samples were enriched in boron-11 in comparison to analyses of detergents and detergent additives reported here (table 9) and in Seiler (2005) and Barth (1998); they were similar to the range reported for sodium borates from California in Oi and others (1989) (table 9).

The boron concentration and boron isotope ratio in the sample from well 3S was similar to domestic-wastewater-affected SA water (fig. 13). Well 3S is about 200 ft from a home along a dune ridge (fig. 7) and may be downgradient from the septic system for that home.

Nitrate or ammonia concentrations of domestic-wastewater-affected SA water from wells 5W, 6W, and 7W indicate that the boron isotope composition of those samples was not affected by mixing with CCP-affected SA water. The results of a hypothetical mixture between CCP-affected SA water and water from well 3S indicate an excess of nitrate in domestic-wastewater-affected SA water from wells 5W and 7W in comparison to each hypothetical mixture (table 10). Similarly, an excess of ammonia was indicated in domestic-wastewater-affected SA water from well 6W in comparison to the hypothetical mixture between CCP-affected SA water and surficial-aquifer water from well 3S. These results indicate that the mixing of less than 0.05 percent of detergent-affected water with water from well 3S would be sufficient to explain boron isotope ratios similar to those reported for domestic-wastewater-affected SA water (table 10).

The larger  $\delta^{11}\text{B}$  of domestic-wastewater-affected SA water, in comparison to detergent sources, likely relates to the composition of surficial-aquifer water and not to adsorption-related fractionation of boron stable isotopes. As discussed previously in relation to sample preservation, the tendency of boron to adsorb onto clays is affected by its speciation in water (Vengosh and others, 1994). The predominant species of boron in water with pH values less than 9.24 is the neutral  $\text{B}(\text{OH})_3^0$  (Palmer and others, 1987; Bassett and others, 1995). The pH of ground water from all wells ranged from 6.2 to 7.85 (table 4). Boron is therefore unlikely to substantially be adsorbed onto clay minerals in this setting because of its predominantly neutral speciation in ground water at these pH values. Boron adsorption would be diminished by the competition for sorption sites between the smaller concentrations of negatively charged  $\text{B}(\text{OH})_4^-$  (about 20 percent of boron in solution at a

pH of 8) with the larger concentrations of other anions such as chloride or sulfate in the same samples.

## Tritium in Representative Ground-Water Sources

Tritium concentrations were used in this report to distinguish between aquifer recharge that postdated 1952 and aquifer recharge that predated 1952 (older ground water, such as that in the basal sand aquifer). For example, recharge to the subfill aquifer and the basal sand aquifer would have longer flow paths through the subsurface than recharge to the surficial aquifer, according to the conceptual hydrogeology (fig. 5) and tritium data (Shedlock and others, 1993). Recharge to the subfill and the basal sand aquifer most likely represent an older source of water.

Tritium concentrations can be used to qualitatively classify ground-water-residence times for continental regions, using the following data ranges, as modified from Clark and Fritz (1997, p. 185).

1. Less than about 0.8 TU—Water represents ground water recharged before 1952 (submodern),
2. 0.8 to about 4 TU—Water represents mixture of submodern and recent (post-1952 recharge),
3. About 4 TU to about 15 TU—Water represents substantially modern recharge (post-1972). Smaller tritium concentrations in this range indicate more mixing with older ground water. Concentration of about 15 TU indicate that there was little or no mixing with older ground water,
4. Greater than about 30 TU—Water contains a significant proportion of synthetic tritium from post-1952 to about 1970 recharge.

Tritium concentrations in ground water were compared with a record of decay-corrected tritium concentrations in precipitation from Ottawa, Canada (International Atomic Energy Agency, 2006), to evaluate similarities and infer a likely range of ground-water age, expressed as the time of recharge (fig. 14). Annual average tritium concentrations were computed for precipitation from the Ottawa site; they were decay corrected to the approximate middle point in time of July 2004, for ground-water sampling done for this investigation by applying a standard decay equation (Clark and Fritz, 1997, p. 181) and the half-life of tritium (12.43 years) (Lucas and Unterweger, 2000). The decay corrected, annual average tritium concentrations in precipitation range from about 10.4 to 19 TU for 1972 and more-recent dates (fig. 14). Therefore, tritium concentrations in ground water derived entirely from a mixture of post-1972 precipitation should be within that range.

Tritium concentrations in six ground-water samples from surficial-aquifer wells 2S, 3S, 4S, 5W, 6W, and 7W ranged from 7.0 TU at well 2S to 10.3 TU at well 5W (table 5; fig. 14). These concentrations were slightly less than or nearly equal to the range of tritium concentrations in decay-corrected post-

**Table 10.** Comparison of chemistry of domestic-wastewater-affected water samples to those from a hypothetical mixture of representative compositions of water from the surficial aquifer and water affected by coal-combustion products.[ $\mu\text{g/L}$ , microgram per liter; B, boron;  $\text{mg/L}$ , milligram per liter; N, as nitrogen; <, less than; concentrations reported as unfiltered constituents except as noted]

Description of representative sample	Representative composition for hypothetical mixture			
	Boron, filtered, unacidified ( $\mu\text{g/L}$ )	$\delta^{11}\text{B}$ , filtered (per mil <sup>1</sup> )	Nitrite plus nitrate ( $\text{mg/L}$ as N)	Ammonia ( $\text{mg/L}$ as N)
Surficial aquifer, well 3S	27	11.2	<0.03	0.05
Coal-combustion product affected water from the surficial aquifer	19,210	2.7, average of four samples (table 5)	< .03, average of three samples (table 5)	2.14, average of four samples (table 5)

Ground-water-sample characteristics			Characteristics of hypothetical mixture of ground water from surficial aquifer (well 3S) and coal-combustion product-affected water from the surficial aquifer					
Sample description	Boron, filtered unacidified ( $\mu\text{g/L}$ )	$\delta^{11}\text{B}$ , filtered (per mil <sup>1</sup> )	Nitrite plus nitrate ( $\text{mg/L}$ as N)	Fraction of mixture from surficial aquifer, well 3S	Fraction of mixture from coal-combustion product affected water	Hypothetical boron concentration in final mixture ( $\mu\text{g/L}$ <sup>1</sup> )	Hypothetical $\delta^{11}\text{B}$ in final mixture (per mil <sup>1</sup> )	Hypothetical nitrite plus nitrate in final mixture ( $\text{mg/L}$ as N <sup>1</sup> )
Well 5W, 04/19/2004	387	11.7	19.7	0.9812	0.0188	387.5	11.1	<0.03
Well 5W, 05/26/2004	373	9.0	19.6	.9818	.0182	376	11.1	< .03
Well 7W, 04/19/2004	84	8.7	1.28	.997	.003	84.5	11.2	< .03

Ground-water sample characteristics			Characteristics of hypothetical mixture of ground water from surficial aquifer (well 3S) and coal-combustion product affected water from the surficial aquifer					
Sample description	Boron, filtered unacidified ( $\mu\text{g/L}$ )	$\delta^{11}\text{B}$ , filtered (per mil <sup>1</sup> )	Ammonia ( $\text{mg/L}$ as N)	Fraction of mixture from surficial aquifer, well 3S	Fraction of mixture from coal-combustion product affected water	Hypothetical boron concentration in final mixture ( $\mu\text{g/L}$ <sup>1</sup> )	Hypothetical $\delta^{11}\text{B}$ in final mixture (per mil <sup>1</sup> )	Hypothetical ammonia concentration in final mixture ( $\text{mg/L}$ as N <sup>1</sup> )
Well 6W, 04/19/2004	98	10.1	1.34	0.9963	0.0037	98	11.2	0.06

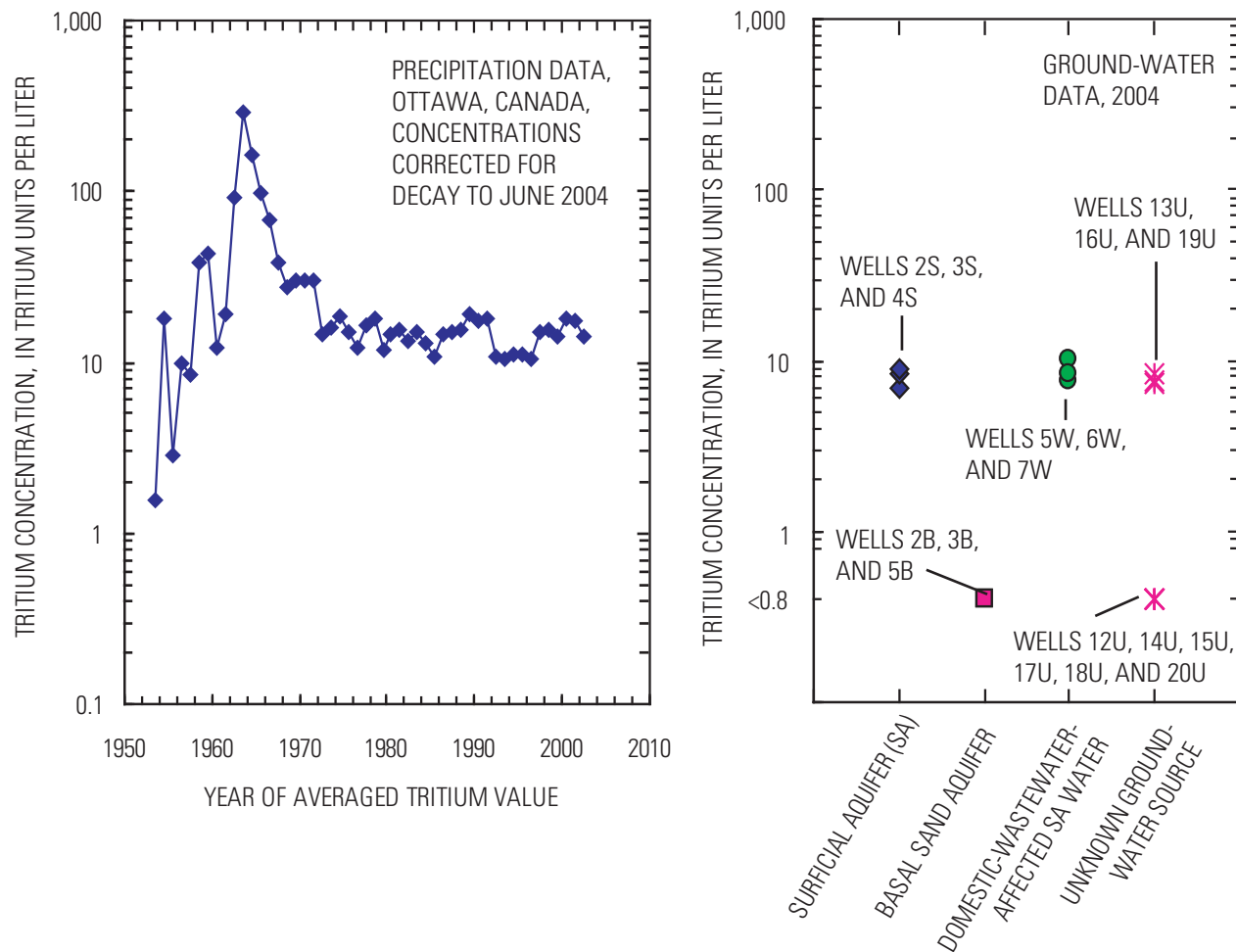
<sup>1</sup>Concentrations of a chemical constituent or ratios of two stable isotopes in hypothetical mixtures were computed, using the formula:

$$A(\text{mixture}) = F(\text{sa}) \times A(\text{sa}) + F(\text{CCP}) \times A(\text{CCP})$$

where:

- A is a chemical constituent  
 F is the fractional volume of an representative composition in a hypothetical mixture  
 sa indicates a characteristic of a sample representing water from the surficial aquifer  
 CCP indicates a characteristic of a sample representing coal-combustion product affected water.

$\delta^{11}\text{B}$  values for the results of hypothetical mixtures were computed, with the ratio of  $^{11}\text{B}/^{10}\text{B}$  for each representative composition in the above equation. The  $^{11}\text{B}/^{10}\text{B}$  of the hypothetical mixture then was converted to  $\delta^{11}\text{B}$  values, in per mil, or the deviation of the  $^{11}\text{B}/^{10}\text{B}$  ratio of the sample from that of a standard material, using the formula:  $\delta^{11}\text{B} = \{[(^{11}\text{B}/^{10}\text{B})_{\text{sample}} - (^{11}\text{B}/^{10}\text{B})_{\text{standard}}] / (^{11}\text{B}/^{10}\text{B})_{\text{standard}}\} * 1000$ ; the standard is NIST-951 boric acid



**Figure 14.** The average annual tritium concentration in precipitation, corrected for decay to July 2004, in samples collected from Ottawa, Canada, 1953–2002 (International Atomic Energy Agency, 2006), compared with tritium concentrations in ground-water samples in the study area near Beverly Shores, northwestern Indiana, 2004.

1972 precipitation (fig. 14). These data indicate that water from wells in the surficial aquifer represents predominantly modern (post-1972) recharge mixed with a smaller amount of submodern (pre-1952) ground water. Seasonal and storm-related ground-water-level rises in the surficial aquifer along the dune-wetland margins (Shedlock and others, 1994, p. 33, 36–38) indicate that modern recharge regularly reaches the surficial aquifer. These ground-water ages indicate that water chemistry from the surficial aquifer is vulnerable to human-affected sources of boron and other constituents.

The lack of detectable tritium (<math><0.8</math> TU) in three basal sand aquifer water samples from wells 2B, 3B, and 5B indicates that source of water and presumably the sources of boron to these wells are associated with pre-1952 recharge not affected by local boron sources. This association presents a strong likelihood that the sources of other dissolved constituents in water including boron from the basal sand aquifer are natural and not human affected. The low tritium concentrations (0.3 to 1.6 TU) identified by Shedlock and others (1993)

in four water samples from the subfill aquifer indicate that the source of boron and other constituents in water from that aquifer predate the disposal of CCP at the Yard 520 landfill.

One explanation for the presence of submodern water in the shallow aquifer is upward flow of water from the confined (subfill or basal sand) aquifers. For example, interpretations of boron isotope data indicate that surficial-aquifer water from well 1S was affected by mixing of surficial-aquifer water and basal sand aquifer water. Water levels in three of four sampled wells (1B, 2B, and 3B) in the basal sand aquifer were above land surface, indicating that parts of the study area are a regional discharge zone for the deeper aquifers. Mixing of recent precipitation with upward flow of older ground water from the confined subfill aquifer was used to explain surficial-aquifer water chemistry at a wetland site about 4.5 mi west of the study area (Shedlock and others, 1993).

Longer flow paths entirely within the shallow aquifer could explain the occurrence of submodern water in the shallow aquifer. Watson and others (2002, fig. 7, p. 25) identified

submodern ground-water ages of two samples at the base of the surficial aquifer (about 30 ft below land surface) in the study area about 400 ft south of wells 2S and 2B. By comparison, ground-water ages in wells screened in the uppermost 10 to 15 ft of the surficial aquifer below the water table were recent (post-1952) and modern (post-1972). The depths of sampled surficial aquifer wells distant from human-affected boron sources ranged from 6.95 to 23.05 ft below land surface (table 2). The previous discussion of boron isotope data, however, indicates that for sampled wells, upward flow from the confined aquifers (basal sand aquifer or subfill aquifer) is a more likely source of the submodern discharge to the shallow aquifer.

### Evaluation of Ground-Water and Boron Sources for Wells with an Unknown Ground-Water Source

Boron concentrations, boron isotope ratios, and tritium concentrations for ground water from six wells with an unknown ground-water source (12U, 14U, 15U, 17U, 18U, and 20U) were similar to those in water from the basal sand aquifer (figs. 15 and 16; table 11). Tritium concentrations in water from those wells were < 0.8 TU and represent ground water recharged before 1952 (table 5; fig. 16). Boron isotope ratios in water from those wells with an unknown ground-water source ranged from 23.8 to 34.7 per mil, similar to the range of ratios from the basal sand aquifer (24.6 to 34.0 per mil) (table 5). The boron isotope and tritium data indicate that the source(s) of ground water and associated boron concentrations to these six wells is not from the recent disposal of domestic-wastewater or CCP residues. This observation is consistent with descriptions that local disposal and use of CCP residues in the Town of Pines area started in about the mid-1960s (ENSR Corporation, 2005).

Samples from wells 14U, 17U, 18U, and 20U contained the only boron concentrations from wells with an unknown ground-water source that were greater than the 900  $\mu\text{g/L}$  USEPA RAL for boron in drinking water (fig. 15). Boron concentrations in water from wells 12U, 14U, 15U, 17U, 18U, and 20U ranged from 436 to 1,920  $\mu\text{g/L}$  (table 5), a range most similar to ground water from deeper, confined aquifers (table 5) (Shedlock and others, 1994, p. 40). The boron isotope and tritium data indicate that water from wells 14U, 17U, 18U, and 20U have a source of boron that is natural and not related to post-1952 contamination; therefore, the RAL does not apply to boron concentrations in water from these wells (table 11).

The tritium concentration in the sample from well 12U (<0.8 TU; table 2) indicates that the source of water and presumably the source of other constituents to this well, such as molybdenum, are associated with pre-1952 recharge (table 11) that predates the disposal of CCP at the Yard 520 landfill. A separate 2004 USEPA sampling of water from well 12U, as referenced in the Introduction, had identified molybdenum in a water sample at a concentration of 10.8  $\mu\text{g/L}$  that is greater

than the 10  $\mu\text{g/L}$  RAL for molybdenum (Kenneth Theisen, U.S. Environmental Protection Agency, written commun., 2007). The source of ground water and the natural source of boron in water from well 12U indicate that the likely source of the large molybdenum concentration was also natural.

Wells 12U and 17U are in an area underlain by the subfill aquifer and basal sand aquifer (Shedlock and others, 1994, p. 26-27) and may produce water from either aquifer. The source of boron and other constituents in water from the subfill aquifer previously were inferred to be natural.

Because no representative samples were analyzed from the subfill aquifer for boron stable isotopes, it was not possible to determine whether the use of boron stable isotopes and tritium could distinguish between water from the subfill and basal sand aquifers.

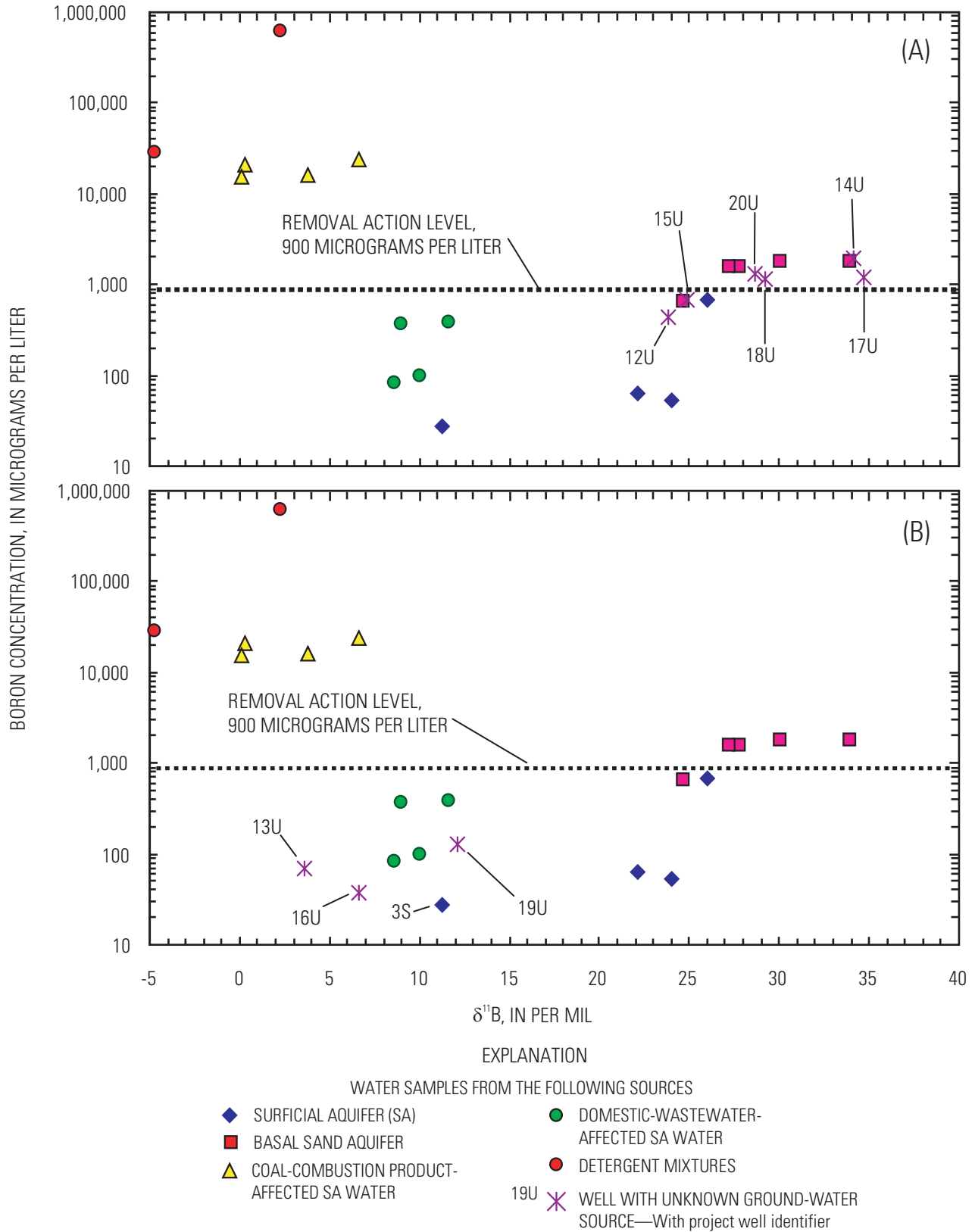
Boron concentrations, boron isotope ratios, and tritium concentrations in water samples from wells 16U and 19U were similar to domestic-wastewater-affected SA water (figs. 15 and 16). The boron isotope ratio for water from well 13U was also similar to those of CCP-affected SA water and detergent mixtures, although the two sources could not be distinguished (table 5; fig. 15). Tritium concentrations in water from wells 13U, 16U, and 19U ranged from 7.4 to 8.4 TU and were within the range of tritium concentrations (7.0 to 10.3 TU) in water from six surficial aquifer wells (2S, 3S, 4S, 5W, 6W, and 7W) (table 5; fig. 16). Concentrations of boron in water from wells 13U, 16U, and 19U ranged from 37  $\mu\text{g/L}$  to 126  $\mu\text{g/L}$  (table 5) and were less than the 900  $\mu\text{g/L}$  USEPA RAL used to regulate boron concentrations in drinking water.

After all water samples were collected, previously unavailable information about well depth was located for wells 12U, 13U, and 15U (table 2). The reported depth for well 15U is 246 ft (Christopher Carlson, Wisconsin Department of Natural Resources, written commun., 2004) and indicates likely production from the basal sand aquifer. Anecdotal information from the land owner at well 12U was that the well is at least 100 ft deep; that depth at this location indicates that this well could produce water from the subfill aquifer, the basal sand aquifer, or both. Tritium data from these wells (table 5) indicate older ground water that would be typical of water from the subfill and basal sand aquifers. By comparison, the reported depth for well 13U is 65 ft (table 2) (Christopher Carlson, Wisconsin Department of Natural Resources, written commun., 2004); the tritium concentration in the sample from well 13U (table 5) indicates water from the surficial aquifer. These comparisons independently verify the effectiveness of the tritium data in assisting to distinguish between ground water produced from the surficial and confined aquifers.

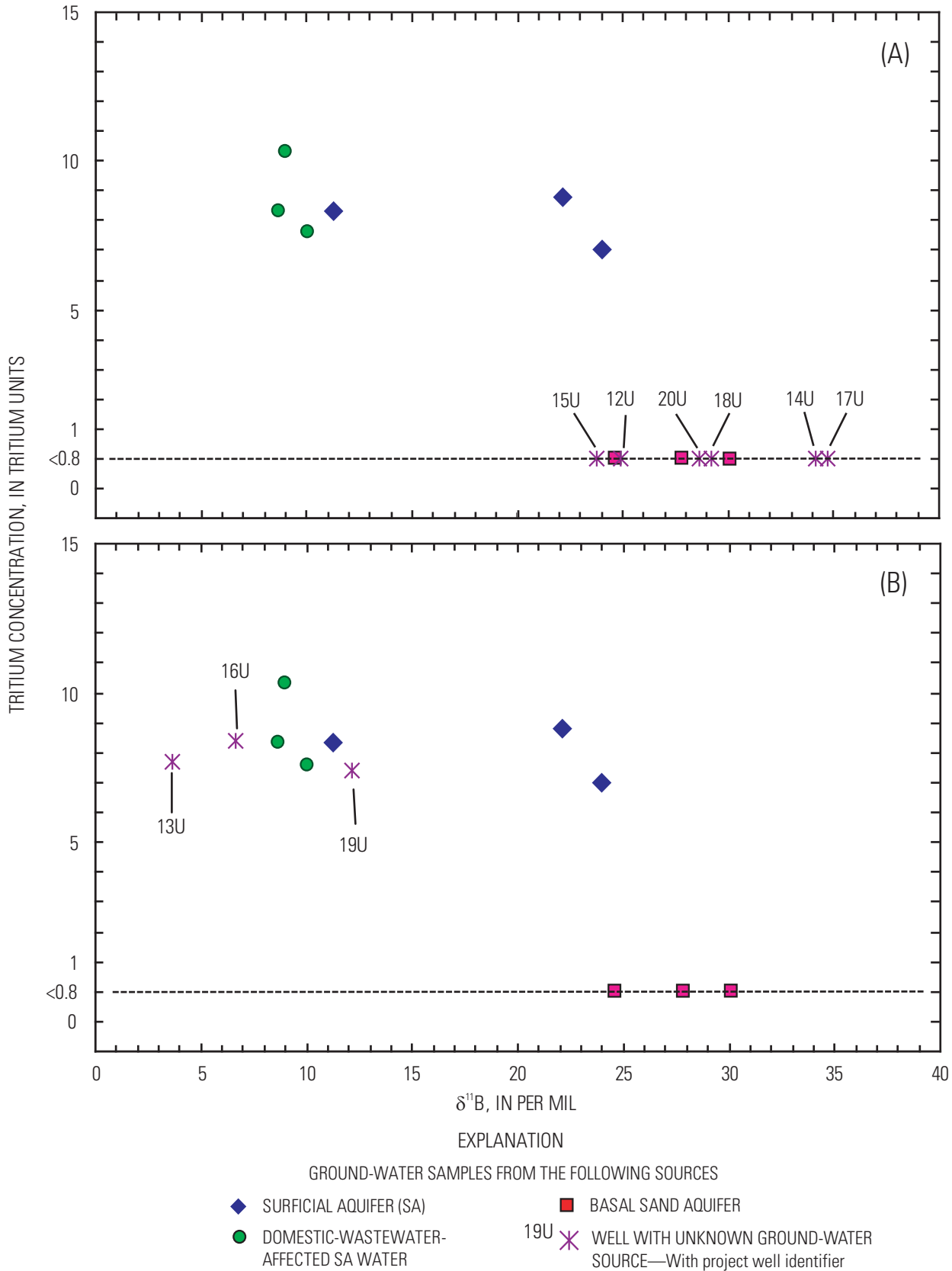
### Comparison with Selected Water-Chemistry Constituents

The results of the classification of ground water and boron sources were compared with other data to indicate any further geochemical similarity of water samples with CCP-





**Figure 15.** Boron concentrations (A) greater than 400 micrograms per liter and (B) less than 200 micrograms per liter in relation to boron isotope composition in water samples from representative sources of boron in ground water and from wells with an unknown ground-water source near Beverly Shores, northwestern Indiana, 2004.



**Figure 16.** Tritium concentrations in water from wells with an unknown ground-water source that were (A) less than 1 tritium unit and (B) greater than 5 tritium units in relation to boron isotope compositions in water samples from representative sources of boron in ground water near Beverly Shores, northwestern Indiana, 2004.

**Table 11.** Classifications of similarity to representative sources of boron in ground water and to ground-water source, based on boron isotope compositions and boron and tritium concentrations.

[USGS, U.S. Geological Survey; USEPA, U.S. Environmental Protection Agency, CCP, coal-combustion product; SA, surficial aquifer]

Project well identifier	USGS station identification number	Date sampled (month/day/year)	Classification of similarity to representative sources of boron in ground water, based on boron isotope ratios and boron concentrations	Classification of similarity to ground-water source, based on tritium concentration	Boron concentration exceeds USEPA removal action level
12U	413953086581801	04/19/2004	Subtill or basal sand aquifer	Submodern water, confined aquifer	No
13U	414052086593201	04/19/2004	CCP-affected SA water or domestic-wastewater-affected SA water	Substantially modern water, surficial aquifer	No
14U	414048086594201	04/19/2004	Basal sand aquifer	Submodern water, confined aquifer	Yes
15U	414050086594001	04/19/2004	Basal sand aquifer	Submodern water, confined aquifer	No
16U	414143086574901	04/19/2004	Domestic-wastewater-affected SA water	Substantially modern water, surficial aquifer	No
17U	414002086581301	11/17/2004	Subtill or basal sand aquifer	Submodern water, confined aquifer	Yes
18U	414106086594701	11/17/2004	Basal sand aquifer	Submodern water, confined aquifer	Yes
19U	414102086595001	11/17/2004	Domestic-wastewater-affected SA water	Substantially modern water, surficial aquifer	No
20U	414103086594501	11/17/2004	Basal sand aquifer	Submodern water, confined aquifer	Yes

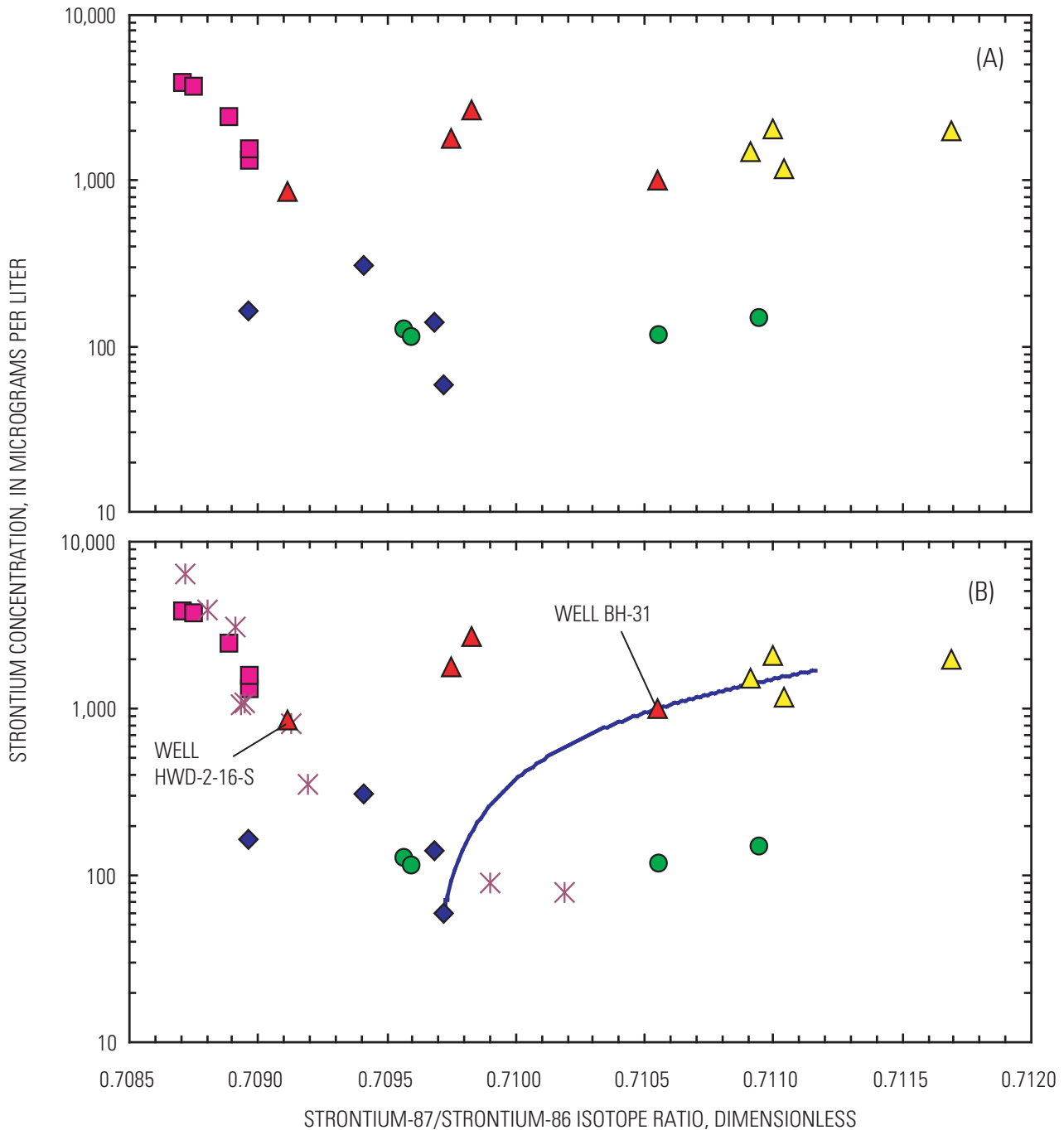
affected and domestic-wastewater-affected SA waters. Other geochemical indicators used for these comparisons included the ratio of strontium isotopes (strontium-87/strontium-86); oxygen stable isotopes; and concentrations of strontium, nitrate, ammonia, and chloride. Inferences about the source of boron derived from the boron and tritium concentrations and boron isotope ratios generally agreed with other geochemical indicators of CCP-affected and domestic-wastewater-affected SA waters.

The strontium-87/strontium-86 ratio has been used to distinguish among several sources of ground-water flow (Gosselin and others, 2004; Bullen and others, 1996); as indicators of water-rock interaction (Bullen and others, 1996); to identify vegetation affected by CCP (fly ash) amendment to soil (Straughan and others, 1981); and to identify sediments affected by slag from steel production (Bayless and others, 2004). The geochemical behavior of strontium is similar to calcium and is affected by sorption and mineral precipitation and dissolution. Strontium-87/strontium-86 ratios of water are not changed by these processes (Gosselin and others, 2004).

Classifications of the likely sources of the ground-water samples from wells with an unknown ground-water source, using strontium-87/strontium-86 ratios and strontium concentrations of representative ground-water sources (fig. 17), were

similar to those obtained with boron and boron isotope ratios (fig. 14). Distinct strontium-87/strontium-86 ratios and strontium concentrations were identified for samples of CCP-affected SA water, domestic-wastewater-affected SA water, and basal sand aquifer water (fig. 17). There was, however, a wide range of strontium-87/strontium-86 ratios in surficial-aquifer water and domestic-wastewater-affected SA water (fig. 17). There is no obvious additional source of strontium in domestic wastewater; therefore the strontium-87/strontium-86 ratio for domestic wastewater may be the same as its original source.

Slag from steel production is used as fill material in northwestern Indiana for road base and aggregate applications and may have been used in the study area (Kay and others, 1997). No comparison was done of slag-affected water quality and other water sources with respect to boron isotope ratios and boron concentrations; a comparison was done instead, using strontium-87/strontium-86 ratios and strontium concentrations. The USGS had analyzed water samples from wells BH-31, BH-32-SL, and BH-33-SL in 1997 and well HWD-2-16-S in 1999 (table 12; fig. 1) from parts of northwestern Indiana outside the study area; the wells were screened in wastes that included slag from steel production (table 12) (Bayless and others, 1998; E.R. Bayless, U.S. Geological Survey, written commun., 2006). The range of strontium-87/strontium-86



- EXPLANATION
- HYPOTHETICAL MIXTURE OF SURFICIAL AQUIFER WATER (WELL S3) AND COAL-COMBUSTION PRODUCT (CCP) AFFECTED WATER
  - GROUND-WATER SAMPLES FROM THE FOLLOWING SOURCES
  - ◆ SURFICIAL AQUIFER (SA)
  - BASAL-SAND AQUIFER
  - WASTEWATER-AFFECTED SA WATER
  - ▲ CCP-AFFECTED SA WATER
  - ▲ SLAG-AFFECTED WATER
  - \* WELL WITH UNKNOWN GROUND-WATER SOURCE

**Figure 17.** Strontium concentrations in relation to strontium-87/strontium-86 isotope ratios in ground-water samples for (A) representative ground-water sources near Beverly Shores, 2004, and slag-affected ground water in northwestern Indiana, 1997–99, and (B) water from wells with an unknown ground-water source near Beverly Shores, 2004.

**Table 12.** Water-chemistry determinations for slag-affected samples collected from wells in northwestern Indiana, 1997 and 1999.[USGS, U.S. Geological Survey; hhmm, hours and minutes;  $\mu\text{g/L}$ , microgram per liter]

Project well identifier (figure 1)	USGS station identification number	Latitude (degrees, minutes, and seconds)	Longitude (degrees, minutes, and seconds)	Date sampled (month/day/year)	Strontium, filtered ( $\mu\text{g/L}$ ) <sup>1</sup>	Strontium-87/strontium-86 ratio, filtered <sup>1</sup>
BH-31	413947087302501	41°39'47"	87°30'25"	07/16/1997	1,000	0.71055
BH-32-SL	413949087301904	41°39'49"	87°30'19"	07/14/1997	2,700	.70983
BH-33-SL	413951087301903	41°39'51"	87°30'18"	07/16/1997	1,800	.70975
HWD-2-16-S	413650087174301	41°36'50"	87°17'43"	02/09/1999	850	.70911

<sup>1</sup>Data source: E.R. Bayless, U.S. Geological Survey (written commun., 2006).

ratios in four samples of slag-affected ground water (table 12) spanned that of CCP-affected SA and basal sand aquifer water samples (fig. 17). One slag-affected water sample that plotted in the region similar to basal sand aquifer water (fig. 17) was produced from well HWD-2-16-S (fig. 1); this well was screened in slag from a basic-oxygen-process steel mill. Tritium concentrations in slag-affected water from wells BH-31, BH-32-SL, and BH-33-SL ranged from 8.0 to 9.1 TU; their ground-water ages were post-1952 (Kay and others, 2002).

Strontium-87/strontium-86 ratios in water samples from wells 12U, 14U, and 17U with an unknown ground-water source were similar to the ratio of a slag-affected water sample from well HWD-2-16-S (fig. 17). The tritium concentrations of samples from wells 12U, 14U, and 17U, however, indicate a submodern ground-water age (table 5). The submodern ground-water-age dates for the samples from wells 12U, 14U, and 17U indicate that the ground-water source for these wells is the confined subsoil or basal sand aquifers. The strontium-87/strontium-86 ratios of ground-water samples from the surficial aquifer, domestic-wastewater-affected SA water, and wells with an unknown ground-water source differ from the ratios of a hypothetical mixture of surficial-aquifer water from well S3 and CCP-affected SA water. These data indicate that shallow aquifer water and domestic-wastewater-affected SA water were not affected by mixing with CCP-affected SA water.

Analyses of 10 water samples for  $\delta^{18}\text{O}$  from wells in the surficial aquifer, domestic-wastewater-affected SA water, and basal sand aquifer indicate some differences between the three representative ground-water sources of boron but not enough to distinguish the surficial-aquifer water from that of the basal sand aquifer. Two samples of domestic-wastewater-affected SA water from well 5W were the most enriched in oxygen-18; with a  $\delta^{18}\text{O}$  of -7.84 and -7.78 per mil (table 5).  $\delta^{18}\text{O}$  values of three samples from the surficial aquifer wells distant from human-affected boron sources were between representative samples of domestic-wastewater-affected SA water and basal sand aquifer water; those values ranged from -8.82 to -8.39 per mil. The shallow aquifer  $\delta^{18}\text{O}$  values were within

published ranges for ground water from unconsolidated geologic materials of northwestern Indiana (-9.30 to -6.66 per mil, Hasenmueller and others, 2001), from the Calumet aquifer in adjacent areas of northwestern Indiana and northeastern Illinois (-11.6 to -5.4 per mil, Kay and others, 2002) and from bedrock units (-19.98 to -8.22 per mil, Hasenmueller and others, 2001). The  $\delta^{18}\text{O}$  values of five samples from wells 1B, 2B, 3B, and 5B ranged from -10.13 to -8.57 per mil (table 5) and were within the range cited for ground water from bedrock units (Hasenmueller and others, 2001).

Nitrate concentrations in two samples of the domestic-wastewater-affected SA water from wells 5W and 7W and in water from well 19U with an unknown ground-water source were greater than 1 mg/L as N (table 5). The nitrate concentrations in two water samples from well 5W (19.7 and 19.6 mg/L as N) exceeded the Federal standard for nitrate in drinking water of 10 mg/L as N (U.S. Environmental Protection Agency, 2006b). Well 5W formerly was used to supply water to an NPS public facility for drinking water and to operate washroom facilities; use of that well was discontinued in 2002 because of large nitrate concentrations (Susan Lehman, National Park Service, oral commun., 2002). There was no known source of boron in the wastewater from the NPS public facility at well 5W. The northward regional direction of ground-water flow in the surficial aquifer (fig. 6) and the domestic-wastewater-affected source of boron in water from that well (fig. 13) make it likely that the nitrate in water from well 5W originated from upgradient homes (fig. 10) and not from wastewater leakage at the NPS public facility.

An ammonia concentration of 1.34 mg/L as N was detected in one sample of domestic-wastewater-affected SA water from well 6W. Ammonia in ground water can originate from domestic wastewater (Verstraeten and others, 2005) ground water in contact with or affected by steel making slag or combined CCP and slag deposits (Bayless and others, 1998), fertilizer, and from natural decay of organic nitrogen (Hem, 1989, p. 125–6). Similarly large ammonia concentrations that ranged from 1.85 to 3.56 mg/L as N were determined for three of the four samples of CCP-affected water

(table 5). The mixing analysis in table 10 indicates a domestic-wastewater-related source of the ammonia in the sample from well 6W.

Chloride concentrations in water samples from the basal sand aquifer (well 3B), domestic-wastewater-affected SA water (wells 5W and 6W), and from wells with an unknown ground-water source (wells 14U, 15U, 18U, and 20U) exceeded the Federal standard for chloride in drinking water (250 mg/L; U.S. Environmental Protection Agency, 2006c) (table 5). The samples from wells 14U, 15U, 18U, and 20U were classified as similar to water from the basal sand aquifer, using information derived from the boron and tritium concentrations and boron isotope ratios (table 11); therefore, the source of the chloride in water from these wells is likely natural. Large chloride concentrations in ground water, however, may originate from other sources such as domestic-wastewater-related discharges of water-softener salt and seepage of road-deicer salt to ground water (Watson and others, 2002). The occurrence of large chloride concentrations in ground water from wells 5W and 6W could have originated from water-softener salt or road-deicer salt; however, the source of chloride in water from wells 5W and 6W is not known.

### Limitations of the Evaluation Method

The evaluations of ground-water sources described for wells sampled are inferences based on the geochemical composition of water samples collected for this investigation. The small number of samples collected to define representative ground-water sources of boron is a potential limitation on wide application of these results. A larger data set may have produced a wider range of isotope values and affected the ability to distinguish chemical differences among samples.

Because no representative samples were collected from the subfill aquifer, potential chemical differences between water from the subfill and deeper aquifers could not be distinguished. If the subfill aquifer was present in the subsurface, wells with an unknown ground-water source that had boron concentrations, boron stable isotope compositions, and tritium concentrations similar to water from the basal sand aquifer were classified as similar to the subfill and basal sand aquifers.

### Summary and Conclusions

Concentrations of boron greater than the 900 µg/L removal action level (RAL) standard were detected in water sampled by the U.S. Environmental Protection Agency (USEPA) in 2004 from three domestic wells near Beverly Shores, Indiana. The RAL only regulates human-affected concentrations of a constituent. A lack of well logs and screened depth information precluded identification of whether water from sampled wells, and their boron sources, were from human-affected or natural sources in the surficial aquifer, or associated with a natural, confined aquifer source of boron

from the subfill or basal sand aquifers. A geochemically-based classification of the source of boron in ground water could potentially determine the similarity of boron to known sources or mixtures between known sources, or classify whether the relative age of the ground water predated the potential sources of contamination. The U.S. Geological Survey (USGS), in cooperation with the USEPA, investigated the use of a geochemical method that applied boron stable isotopes, tritium, and other constituents to distinguish between natural and human-affected sources of boron in ground water and thereby determine if the RAL was applicable to the situation.

Water samples were collected from four wells in parts of the surficial aquifer (SA) distant from boron sources, four wells in the basal sand aquifer, four wells in the SA with coal-combustion product (CCP) affected water chemistry and three wells in the SA with domestic-wastewater-affected water quality. Nine additional water samples were collected from one public-supply well and eight domestic-supply wells where the well depth and ground-water source were not known when they were sampled (classified as from an "unknown ground-water source"). Water samples were analyzed for concentrations of boron (26 samples), chloride (24 samples), sulfate (24 samples), ammonia as nitrogen (26 samples), nitrite plus nitrate as nitrogen (26 samples), and strontium (26 samples). Water samples also were analyzed for the stable isotope ratios  $\delta^{11}\text{B}$  (boron-11/boron-10) (26 samples) and  $\delta^{18}\text{O}$  (oxygen-18/oxygen-16) (10 samples), for ratios of the decaying isotope strontium-87 to the stable isotope strontium-86 (strontium-87/strontium-86) (26 samples), and for concentrations of the decaying isotope, tritium (hydrogen-3; 18 samples).

Boron concentrations in potential ground-water sources of boron were largest (15,700 to 24,400 µg/L) in samples of CCP-affected SA water from four wells (8A, 9A, 10A and 11A) at a CCP landfill (the Yard 520 landfill) and smallest (27 to 63 µg/L) in three of four wells (2S, 3S, and 4S) in the SA that were distant from human-affected boron sources. Boron concentrations in water from the basal sand aquifer ranged from 656 µg/L in a sample from well 2B to 1,800 µg/L in a sample from well 3B. Boron concentrations in water from three domestic-wastewater-affected SA wells (5W, 6W and 7W) ranged from 84 to 387 µg/L.

The largest boron isotope ratios, ranging from 24.6 to 34.0 per mil were in water from the basal sand aquifer. The smallest boron isotope ratios among representative ground-water sources of boron, ranging from 0.1 to 6.6 per mil were in CCP-affected SA water. Boron isotope ratios in domestic-wastewater-affected SA water ranged from 8.7 to 11.7 per mil; these values were between those of CCP-affected SA water and basal sand aquifer water. Boron isotope ratios in analyses of prepared samples of a borax detergent additive and a detergent with sodium perborate bleach were similar to or less than those of CCP-affected SA water. Tritium concentrations ranged from 7.0 to 10.3 tritium units (TU) in six surficial aquifer samples and were <0.8 TU in three basal sand aquifer samples. Similarities between a ground-water sample from the SA and a hypothetical mixture between SA and basal sand

aquifer waters indicate the potential for long-term upward discharge of ground water into the SA from one or more confined aquifers.

Boron and  $\delta^{11}\text{B}$  analyses for this investigation were made on unacidified samples to assure consistency of the result with unacidified analyses of  $\delta^{11}\text{B}$  values from other investigations. A comparison of boron concentrations in acid-preserved and unacidified samples indicated that boron concentrations reported for this investigation may be from about 11 to 16 percent less than would be reported in a standard analysis of an acidified sample. Estimated  $\delta^{11}\text{B}$  values for acidified samples were depleted by 1.9 to 2.8 per mil in comparison to unacidified samples from the four wells sampled; those differences were small in comparison to the differences between  $\delta^{11}\text{B}$  values of representative ground-water sources of boron.

Boron concentrations, boron isotope ratios, and tritium concentrations in ground-water samples from five domestic wells (14U, 15U, 17U, 18U, and 20U) and one public-supply well (12U) where the ground-water source was unknown were similar to submodern water from the basal sand aquifer. Boron concentrations in water from four (14U, 17U, 18U, and 20U) of the six wells were greater than the USEPA RAL of 900  $\mu\text{g/L}$ . The boron isotope and tritium data from these four wells (14U, 17U, 18U, and 20U) indicate a source of boron in ground water that is natural and not related to post-1952 contamination; therefore, the RAL does not apply to boron concentrations in water from these wells. Wells 12U and 17U are in an area underlain by the subfill aquifer and basal sand aquifer. Because no water samples were analyzed from the subfill aquifer for boron stable isotopes, it was not possible to determine whether the use of boron stable isotopes and tritium could distinguish between water from the subfill and basal sand aquifers.

In water samples from two domestic wells (16U and 19U) where the ground-water source was unknown, boron concentrations were less than the RAL; boron isotope ratios and tritium concentrations were similar to domestic-wastewater-affected SA water. The boron isotope ratio for a sample from one domestic well (13U) was similar to those of CCP-affected SA water and detergent compositions. The two sources could not be distinguished for well 13U; the boron concentration of that sample, however, was less than the RAL. These classifications of differences among samples of representative ground-water sources of boron and their similarities to water samples from wells where the ground-water source was unknown generally agreed with distinctions identified using strontium-87/strontium-86 ratios and concentrations of strontium, chloride, nitrate, and ammonia.

Major conclusions of this study are summarized below:

- A geochemically-based classification using boron concentrations, boron stable isotope ratios, and tritium was able to distinguish between boron from natural sources and from human-affected sources that are subject to regulation.

- The boron isotope ratios ( $\delta^{11}\text{B}$ ) were largest in a natural source of boron (basal sand aquifer water), and smallest in two possible human-affected sources of boron in ground water (CCP-affected SA water and boron detergent additives). The  $\delta^{11}\text{B}$  of wastewater-affected surficial aquifer water was intermediate between basal sand aquifer water and the above human-affected sources of boron in ground water.
- Tritium concentrations indicate that water from the basal sand aquifer is associated with pre-1952 recharge from sources not affected by local boron inputs. Tritium concentrations also indicate that water from wells in the SA represent predominantly post-1972 recharge and therefore from post-1972 sources of boron and other constituents.
- Ground water with boron concentrations greater than the USEPA RAL of 900  $\mu\text{g/L}$  for drinking water from wells where the ground-water source was unknown had boron isotope ratios and tritium concentrations that indicate a source of boron that is natural. Therefore, the RAL does not apply to boron concentrations in water from these wells.
- Ground water with boron concentrations less than the USEPA RAL from wells where the ground-water source was unknown had boron isotope ratios and tritium concentrations similar to human-affected sources (wastewater-affected SA water or CCP-affected SA water).

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