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

Diel Sampling of Groundwater and Surface Water for Trace Elements and Select Water-Quality Constituents at a Former Zinc Smelter Site near Hegeler, Illinois, August 1–3, 2007

Scientific Investigations Report 2009–5210

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

Cover: Grape Creek, near Hegeler, Illinois, looking west; U.S. Geological Survey streamgage SW1 is in foreground. (Photograph by Heather J. Rosenfeld, U.S. Environmental Protection Agency, August 1, 2007)

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KEN SALAZAR, Secretary

U.S. Geological Survey
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Conversion Factors

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
gallon (gal)	3.785	liter (L)

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

°F=(1.8×°C)+32

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Altitude, as used in this report, refers to distance above or below NAVD 88.

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Abbreviated water-quality units: Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L). Milligrams per liter are considered equivalent to parts per million at the reported concentrations. Micrograms per liter are considered equivalent to parts per billion at the reported concentrations.

Abbreviated soil- and sediment-quality units: Chemical concentration is given in metric units. Chemical concentration is given in milligrams per kilogram (mg/kg). Milligrams per kilogram is a unit expressing the concentrations of chemical constituents as weight (milligrams) of the constituent per unit mass (kilogram) of soil or sediment. One kilogram equals 1,000,000 milligrams.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Oxidation-reduction potential is given in millivolts (mv).

The measurement of the mesh size of some sampling devices is measured in microns, which also are known as micrometers; one micron is equivalent to one-thousandth of a millimeter.

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Abstract

Surface water can exhibit substantial diel variations in the concentration of a number of constituents. Sampling regimens that do not characterize diel variations in water quality can result in an inaccurate understanding of site conditions and of the threat posed by the site to human health and the environment. Surface- and groundwater affected by acid drainage were sampled every 60 to 90 minutes over a 48-hour period at a former zinc smelter known as the Hegeler Zinc Superfund Site, in Hegeler, Ill. Groundwater-quality data from a well at the site indicate stable, low pH, weakly oxidizing geochemical conditions in the aquifer. With the exceptions of temperature and pH, no constituents exhibited diel variations in groundwater. Variations in temperature and pH likely were not representative of conditions in the aquifer.

Surface water was sampled at a site on Grape Creek. Diel variations were observed in temperature, dissolved oxygen, pH, and specific conductance, and in the concentrations of nitrite, barium, iron, lead, vanadium, and possibly uranium. Concentrations during the diel cycles varied by about an order of magnitude for nitrite and varied by about a factor of two for barium, iron, lead, vanadium, and uranium. Temperature, dissolved oxygen, specific conductance, nitrite, barium, lead, and uranium generally reached maximum values during the afternoon and minimum values during the night. Iron, vanadium, and pH generally reached minimum values during the afternoon and maximum values during the night. These variations would need to be accounted for during sampling of surface-water quality in similar hydrologic settings.

The temperature variations in surface water were affected by variations in air temperature. Concentrations of dissolved oxygen were affected by variations in the intensity of photosynthetic activity and respiration. Nitrite likely was formed by the oxidation of ammonium by dissolved oxygen and degraded by its anaerobic oxidation by ammonium or as part of the decomposition of organic matter. Variations in pH were affected by the photoreduction of Fe^{3+} to Fe^{2+} and the precipitation of iron oxyhydroxides. Diel variations in concentrations of iron and vanadium were likely caused by variations in the dissolution and precipitation of iron oxyhydroxides, oxyhydroxysulfates, and hydrous sulfates, which may have been affected by in the intensity of insolation, iron photoreduction, and the concentration of dissolved oxygen. The concentrations of lead, uranium, and perhaps barium in Grape Creek may have been affected by competition for sorption sites on iron oxyhydroxides. Competition for sorption sites was likely affected by variations in pH and the concentration of Fe^{2+}. Constituent concentrations likely also were affected by precipitation and dissolution of minerals that are sensitive to changes in pH, temperature, oxidation-reduction conditions, and biologic activity. The chemical and biologic processes that resulted in the diel variations observed in Grape Creek occurred within the surface-water column or in the underlying sediments.

Introduction

Stream-water samples collected for Superfund and other environmental investigations typically are single samples collected at a convenient time during the working day for the person who collects the samples. These samples form the basis for decisions about the threat posed by a site to human health and the environment as well as the efficacy of remedial actions. Evaluation of this data implicitly assumes that constituent concentrations in the sample are representative of worst case or, at least, typical conditions in the stream. In many instances this assumption is not valid because concentrations of a number of constituents may vary substantially on a diel basis, which is a daily cycle occurring over a 24-hour period.

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Diel variations in concentrations of chemical constituents have been observed in surface water. For example, diel variations in geochemical-indicator parameters, such as pH, dissolved oxygen (DO), temperature, and nitrite, have been observed in Illinois and Indiana streams in the summer months (Groschen and King, 2005; Antweiler and others, 2005). Concentrations of DO and pH values typically were at their lowest at approximately 1000 hours, increased until approximately 2200 hours, then decreased throughout the night and early morning (times from other investigations are those presented in the reports, whereas times from this investigation are presented in Central Daylight Saving time). Diel variations in concentrations of nitrite, when observed, showed an inverse relation to DO.

Diel variations in the concentrations of several trace elements were measured in many pH-neutral to alkaline streams draining mining areas in western Montana and Idaho during the summer months (Brick and Moore, 1996; Nimick, 2003). These studies determined that concentrations of dissolved cadmium, manganese, and zinc differed by 210 to 590 percent during a 24-hour period. Concentrations of these metals were highest shortly after sunrise, decreased to minimum values during mid- to late afternoon, and then began to increase. Arsenic showed an opposite trend, with total differences in concentration of up to 50 percent. Later investigations (Nimick and others, 2005) determined that diel variations persist throughout the year. Diel variations in the concentrations of iron and other trace elements also have been observed in acidic surface water in Colorado and Montana (McKnight and Bencala, 1988; McKnight and others, 1988; Gammons and others, 2005a,b). Concentrations of iron differed by as much as 500 percent and were highest during the day and lowest at about midnight.

Diel variations in concentrations of various constituents in streams occur in response to changes in temperature, pH, and the intensity of incident sunlight (Nimick and others, 2003; Jones and others, 2004). Diel variations in the amount of incident solar radiation (insolation) affect the intensity of photosynthesis, which can be represented by the equation

$$CO_2 + H_2O + \textit{photons} => CH_2O + O_2 \qquad (1)$$

Organic matter is represented by CH_2O. Respiration, which is the decomposition of organic matter, occurs at night. Respiration is represented as the reverse of equation 1, without the generation of photons. Respiration is accompanied by an additional, reversible step in which carbon dioxide and water produce bicarbonate and hydrogen ions.

$$CO_2 + H_2O \Leftrightarrow HCO_3^- + H^+ \qquad (2)$$

Thus, photosynthesis can cause an increase in pH and in concentrations of DO, whereas respiration decreases pH and DO.

The concentration of DO, often with the assistance of bacteria, also can affect concentrations of other constituents, for example, by removing iron from the water column during the precipitation of goethite (equation 3) or changing the form of the nitrogen compounds during ammonium oxidation (equation 4).

$$Fe^{2+} + 0.25O_2 + 1.5\ H_2O \Leftrightarrow FeO(OH) + 2H^+ \qquad (3)$$

$$NH_4^+ + 1.50_2 \Leftrightarrow NO_2^- + 2H^+ + H_20 \qquad (4)$$

Diel variations in the amount of insolation also affect the intensity of photoreduction (chemical reactions induced by solar radiation) and the intensity of some chemical reactions in the water column (McKnight and others, 1988). For example, photoreduction of iron sulfate complexes, expressed as

$$Fe(SO_4)^+ + 0.5\ H_2O \Leftrightarrow Fe^{2+} + SO_4^{2-} + H^+ + 0.5O_2 \qquad (5)$$

has been postulated (Gammons and others, 2005a).

Similarly, changes in temperature, concentration of DO, and insolation also influence the activity of various microbiological communities in the water column and sediments. Differences in biologic activity result in diel variations in geochemical conditions in the water column and underlying sediments that affect the equilibrium solubility of many constituents, including trace elements (Fuller and Davis, 1989; Nimick and others, 2003; Parker and others, 2005; Gammons and others, 2005a,b).

Although diel variations in concentrations of trace elements have been identified in the western United States, it was unknown if such differences occur in Midwestern streams, which can have substantially different climatic, hydraulic, and geochemical characteristics. In addition, diel variations in concentration have been reported for a relatively few metalloids (primarily iron, copper, manganese, arsenic, cadmium, and zinc) and geochemical indicators, such as pH and DO. The potential for diel variations in concentrations of other constituents, such as mercury (Nimick and others, 2007), and rare earth elements (Gammons and others, 2005b) has been less intensively investigated. Previous investigations have focused on water quality in streams, but the authors are not aware of any investigations in which concurrent diel sampling of groundwater quality was performed to determine if diel variations in chemistry (if any) of recharging groundwater can cause diel variations in surface-water quality. Finally, many of the previous investigations have monitored ambient water quality in mining districts, but they have not focused on those parts of the streams in the immediate area of waste materials. It is possible that constituent concentrations in severely affected waters are so high that diel variations are too small to be clearly identified or that important biologic communities are too severely affected to cause distinct water-quality changes.

To assess the potential for diel variations in concentrations of dissolved trace elements and other constituents in surface- and groundwater at Midwestern Superfund sites, the U.S. Geological Survey (USGS) Illinois Water Science Center conducted an investigation, in cooperation with the U.S. Environmental Protection Agency, to identify and characterize diel variations in surface- and groundwater quality at the Hegeler Zinc Superfund site near Hegeler, Ill. (fig. 1). This site, hereafter referred to as the Hegeler Zinc site, is the location of a former zinc smelter that operated from 1907 through 1947. Disposal of slag and other types of waste fill material at this site has resulted in low pH, high sulfate water that is similar to severe acid mine drainage and toxic or near-toxic concentrations of trace elements in soil, sediment, surface water, and groundwater.

Purpose and Scope

This report is an assessment of diel variations in surface-water and groundwater chemistry in an area affected by fill materials from a zinc smelting operation near the town of Hegeler, Ill. The report presents a compilation of site history, geology, surface-water and groundwater hydrology, as well as surface-water and groundwater quality at the site. Included are the analyses of 48 surface-water samples and 32 groundwater samples collected during a 48-hour period from August 1 through 3, 2007. In addition, results of chemical modeling of the water-quality data are presented. These analyses were performed to determine the presence, timing, and magnitude of diel variations in water quality at the site and to determine the processes that affect these variations. It is anticipated that the results of this investigation can be used to help determine if diel variations in water quality are substantial enough to warrant modifications to standard surface- and groundwater sampling procedures for environmental investigations as well as the form those modifications should take.

Description of the Hegeler Zinc Site

In addition to zinc smelting, coal mining, sulfuric acid production, and cadmium processing also occurred at the site during some or all of the operating period (1907–47). Smelter slag and other solid materials generated from site operations were disposed of as fill throughout the site, including in a large slag pile in the southern part of the site (fig. 1).

Geologic Units and Hydrology

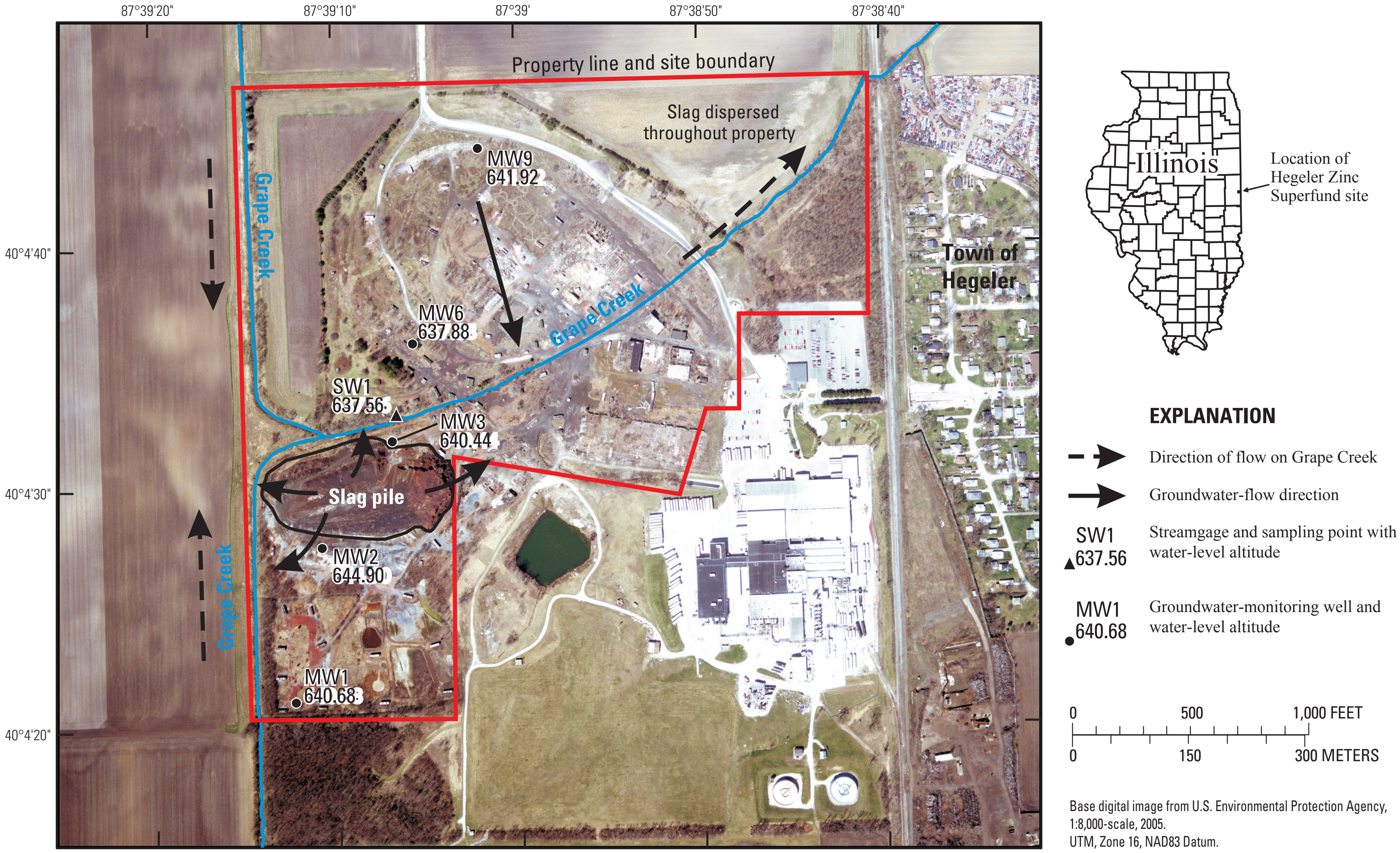
The geologic units of concern to this investigation are the surficial fill and the underlying glacial drift. Fill deposits are primarily of smelter slag, with smaller amounts of scrap metal, coal mine spoil, coal ash, and demolition debris. Fill deposits range in thickness from 1 to 12 ft beneath most of the site, and typically thicker deposits are near the creek (Roy F. Weston, Inc., 2007). Fill deposits are as much as 54 ft above the surrounding landscape at the slag pile. Glacial deposits are mostly silt and clay till, with lenses of sand and gravel locally. Glacial deposits are more than 50 ft thick beneath the site.

The water table typically is within the fill south of the creek and within the glacial deposits north of the creek (Roy F. Weston, Inc., 2007). Water-level measurements collected during the sampling period (table 1) and previous studies indicate that shallow groundwater beneath the site flows toward, and discharges into, Grape Creek (fig. 1). Water levels also may indicate a water-table mound beneath the slag pile. Groundwater discharge to the creek has been confirmed by flowing seeps near staff gage SW1 observed during previous investigations (Roy F. Weston, Inc., 2007). Water was observed at the stream bank at one of the seep locations near staff gage SW1 during the sampling period, but it had no observable flow.

Grape Creek is a channelized perennial stream that borders the site to the southwest and northwest, where it drains an agricultural area (fig. 1). The drainage area of the creek at staff gage SW1 is 4.08 mi^2. The two branches join near the western-central part of the site and flow through the center of the site to the east-northeast. The creek typically is about 10 ft wide and less than 1 ft deep and is lined by trees near and upstream of gage SW1 that shade much of the reach (see picture on front cover). Filamentous and other algae were observed on the creek sediments and floating on the water surface during sampling. The sediment at gage SW1 is a poorly consolidated mixture of sand and silt. The creek is in direct contact with fill material in the study reach and does not receive wastewater discharge upstream of gage SW1. During the sampling period Grape Creek was under base-flow conditions, but no flow was observed in the creek.

Previous Analyses of Metals in Soils, Stream Sediments, Groundwater, and Streamwater

Waste disposal at the site has resulted in the presence of substantial concentrations of inorganic constituents in soil, sediment, surface water, and groundwater in and near the site (Roy F. Weston Inc., 2007). Antimony (maximum concentration about 830 mg/kg), arsenic (720 mg/kg), cadmium (710 mg/kg), iron (140,000 mg/kg), cobalt (28 mg/kg), copper (1,100 mg/kg), lead (72,100 mg/kg), mercury (2,000 mg/kg), selenium (610 mg/kg), and zinc (78,000 mg/kg) were detected in the upper 6 in. of site soils. Arsenic (maximum concentration 49 mg/kg), cadmium (20 mg/kg), copper (510 mg/kg), iron (135,000 mg/kg), lead (6,550 mg/kg), mercury (9.6 mg/kg), nickel (28 mg/kg), and zinc (9,000 mg/kg) were detected in sediments from Grape Creek at and downstream of the site. Aluminum (maximum concentration 66 mg/L), cadmium (3.4 mg/L), iron (130 mg/L), manganese (8.1 mg/L), and zinc (200 mg/L) were detected in groundwater beneath the site. Cadmium (maximum concentration 3.7 mg/L), iron (240 mg/L), manganese (8.6 mg/L), and zinc (170 mg/L) were detected in water samples from Grape Creek at and downstream of the site.



Base digital image from U.S. Environmental Protection Agency, 1:8,000-scale, 2005.
UTM, Zone 16, NAD83 Datum.

Figure 1. Aerial photograph of the Hegeler Zinc Superfund site, near Hegeler, Illinois, showing site location, select features, and water levels on August 1, 2007.

Table 1. Well, streamgage, and stream-sediment sample information at the Hegeler Zinc Superfund site, near Hegeler, Illinois. (Locations of wells and streamgages are shown on figure 1.)

[NAVD88, North American Vertical Datum of 1988]

Well identifier	Latitude/longitude	Altitude, top of inner casing (feet above NAVD88)	Land-surface altitude (feet above NAVD88)	Depth of open interval (feet below land surface)	Water-level altitude, August 1, 2007 (feet above NAVD88)
MW1	40º04’22”/87º39’13”	649.73	646.7	3–13	640.68
MW2	40º04’27”/87º39’10”	651.03	647.8	2.5–12.5	644.90
MW3	40º04’33”/87º39’05”	648.66	645.8	5–15	640.44
MW6	40º04’37”/87º39’05”	649.42	646.0	5–15	637.88
MW9	40º04’44”/87º39’04”	650.12	646.6	3–13	641.92

Streamgage	Latitude/longitude	Altitude of reference point (feet above NAVD88)	Water-level altitude August 1, 2007 (feet above NAVD88)
SW1	40º04’34”/87º39’04”	638.74	637.56

Stream-sediment sample identifier	Latitude/longitude
IL-HG-1-SS	40º04’34”/87º39’05”
IL-HG-2-SS	40º04’34”/87º39’04”

Climatic Conditions During the Sampling Period

Air temperature, solar radiation, and precipitation before and during the sampling period were obtained from the National Climatic Data Center (NCDC) station in Bondville, Ill. (*http://www.ncdc.noaa.gov/crn/hourly?station_id=1037*, accessed January 9, 2008). Bondville is approximately 30 mi due west of the site. Temperature and precipitation conditions at Bondville were similar to those measured at the NCDC station at the Vermillion County Airport (*http://cdo.ncdc.noaa.gov/qclcd/QCLCD*, accessed January 9, 2008), which is located about 6 mi north of the site. Climate data for Bondville are used in this report because they are more detailed and because data on solar and photosynthetically active radiation were not collected at the Vermillion County Airport.

Air temperature measured at Bondville during the sampling period ranged from 16.7 to 30.3°C (fig. 2). The highest temperatures were measured in the afternoon and early evening between about 1300 and 1700 hours. The lowest temperatures were measured in the morning at about 0600 hours.

The net values of solar radiation measured at Bondville during the sampling period ranged from 0 to 912 watts/m^2 (fig. 2). Solar radiation values peaked at about 1300 to 1400 hours. Solar radiation was not detected between sunset at about 2005 hours and sunrise at about 0550 hours. Values of photosynthetically active radiation were about one-half of the net values. Cloud cover was minimal during the sampling period and had negligible effect on the amount of solar radiation hitting the creek. The shade from the tree canopy likely did not substantially affect the intensity of the solar radiation hitting the creek, but it did reduce the total amount of radiation reaching the creek.

No rain fell at or near the site during the sampling period. The most recent rain event measured at the Bondville and Danville stations prior to the sampling period was 0.51 in. measured on July 27, 2007. That rainfall had no observable effect on flow or water levels in Grape Creek during the sampling period.

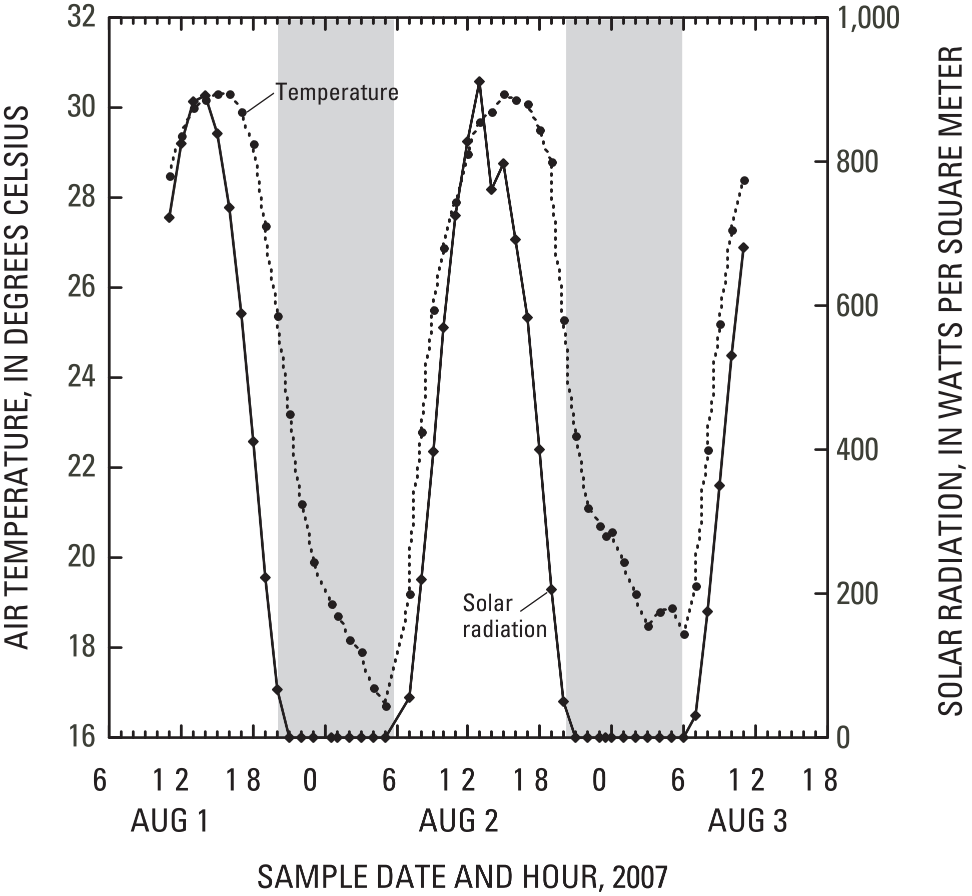


Figure 2. Air temperature and solar radiation measured at the National Climatic Data Center station, Bondville, Illinois, August 1–3, 2007. (Gray bars indicate night.)

Approach and Methods of Investigation

Approach

Groundwater quality was determined by collection of samples from well MW3. Well MW3 is located between the slag pile and Grape Creek (fig. 1), which makes it ideal for assessing water quality impacted by slag materials. Stream-water quality was determined by collection of samples from staff gage SW1, which is located at a point where groundwater that is highly impacted by waste deposition enters the creek. Samples were collected during base-flow conditions in August because it was anticipated that the conditions that affect diel variations in water quality, such as variations in solar radiation, water temperature, and photosynthetic activity, would be most pronounced during these hydrologic and climatic conditions. Samples were collected during a 48-hour period to determine if cycles observed on one day were repeated.

Field Parameters and Sample Collection

Groundwater samples were collected from monitoring well MW3 (fig. 1) every 90 minutes from 1245 hours on August 1, 2007, through 1115 hours on August 3, 2007. Well MW3 has a screen length of 10 ft, which was almost fully saturated at the time of sampling (table 1). A peristaltic pump was used to purge and sample the well, and its Teflon tube intake was placed approximately 3 ft above the bottom of the well screen to ensure collection of a representative sample. Water temperature, pH, DO, oxidation-reduction potential (ORP), and specific conductance (hereafter referred to as the field parameters) were measured during pumping by use of a calibrated Yellow Springs Instruments 556 meter with an in-line flow-through cell. Samples were observed to be clear and colorless with no visible particulate matter. Samples for laboratory analysis were collected after 5 gal of water, which represented three well volumes, had been purged and monitoring had established that the field parameters were stable. Values of field parameters were recorded immediately prior to sample collection.

Water samples were collected from Grape Creek near staff gage SW1 (fig. 1) every 60 minutes from 1115 hours on August 1, 2007, through 1115 hours on August 3, 2007 (hereafter referred to as the sampling period). Stream samples were collected by use of a peristaltic pump, which pumped water through Teflon tubing. The intake tube for the pump was attached to a PVC rod inserted into the streambed. The intake was placed in the middle of the water column in the creek to ensure collection of a representative sample.

Field parameters were measured in Grape Creek at SW1 by use of a second calibrated Yellow Springs Instruments 556 water-quality meter attached to a wood stake located within 2 ft of the pump intake. The sonde sensors were positioned mid-depth in the water column. Values of field parameters in Grape Creek typically were recorded every 15 minutes, although problems with the instrument sometimes necessitated a longer period between measurements.

Water samples submitted for laboratory analysis were placed in clean bottles to which preservative (as appropriate) had already been added, immediately stored on ice in a cooler, and delivered to the laboratory within 72 hours of collection. Samples requiring filtration were filtered with 0.45-micron pore size in-line capsule filters at the discharge point of the tubing for the peristaltic pumps.

Analytical Methods

Samples were analyzed in the laboratory for a suite of trace elements, major ions, nitrate plus nitrite as nitrogen, and nitrite as nitrogen. Select samples from Grape Creek also were analyzed for mercury. All laboratory analyses were performed by the USGS National Water-Quality Laboratory in Denver, Colo. Cations were analyzed by use of inductively coupled plasma (ICP) or inductively coupled plasma with mass spectrometry (ICP-MS; Faires, 1993; Garbarino, 1999). Sulfate and chloride were analyzed by use of ion chromatography (Fishman and Friedman, 1989). Mercury was analyzed by use of cold-vapor atomic fluorescence (Garbarino and Damrau, 2001). Nitrogen compounds were analyzed by use of colorimetric techniques (Fishman and Friedman, 1989).

Quality Assurance and Quality Control

All sampling and lab analyses were done in accordance with the Quality-Assurance Project Plan (QAPP) and Field Sampling Plan developed for this investigation. Copies of the Field Sampling Plan and QAPP are available upon request from the USGS Illinois Water Science Center. An equipment blank was collected in the field before the start of sampling from the peristaltic pump and tubing used to sample Grape Creek. Duplicate samples were collected at a frequency of 1 for every 10 investigative samples. Appropriate laboratory matrix spike and matrix spike duplicate (MS/MSD) analyses were performed. Per the QAPP, no MS/MSD samples were collected or analyzed in the field.

Analyses above and beyond the requirements of the QAPP were performed to ensure the quality of the data. The charge balance for each sample was computed by use of the PHREEQC model (Parkhurst and Appelo, 1999) to assess the overall completeness and quality of the analyses. Ideally, the charge balance should be near zero. The charge balance is computed by summing the cations and anions as equivalents (molar concentrations multiplied by the ionic charge). PHREEQC calculates the equivalent value of the various species of cations and anions from the pH, temperature, redox state, ionic strength, and input analytical concentrations for the solution. Concentrations of DO were used to determine the redox conditions of the sample. The dilution factor and date of analysis were analyzed for all constituents that exhibited more than a 30 percent change in concentration during the sampling to assess the potential affect of laboratory artifacts on the results.

Statistics and Geochemical Modeling

The concentrations of each constituent, including field parameters, detected in at least 70 percent of the water samples from Grape Creek or MW3 were plotted against each other, and the square of the Pearson product-moment correlation coefficient (R^2) for each constituent pair was calculated by use of Microsoft Excel. Constituents detected in fewer than 70 percent of the samples from Grape Creek or MW3 were not analyzed. Nondetects were plotted at one-half the lowest concentration detected for the constituent at that sample location.

Arithmetic mean concentrations were calculated for constituents detected in Grape Creek or in well MW3 at a frequency of greater than 69 percent. Arithmetic mean concentrations for constituents detected at a frequency from 70 to 99 percent were estimated by use of the Kaplan-Meier method (Helsel, 2005). Arithmetic mean concentrations for constituents detected in every sample were calculated by use of the average function in Excel.

Results from every water sample were modeled to determine the distribution of dissolved species and saturation indices of minerals known or considered likely to be present in the fill, geologic deposits, and stream sediments at the site. Saturation index is defined as the log of the ratio of the ion activity product in the sample to the solubility product (Ksp) constant of a specific mineral. Speciation and saturation indices were computed by use of PHREEQC (Parkhurst and Appelo, 1999) and referenced the WATEQ4F (Ball and Nordstrom, 1991) or Lawrence Livermore National Laboratory (Delany and Lundeen, 1990) thermochemical databases. PHREEQC also was used to determine the charge balance of each of the samples.

Collection of Hydrologic Data

Water levels were measured in select monitoring wells and at staff gage SW1 on August 1, 2007, to determine hydraulic conditions at the time of sampling (fig. 1; table 1). Water-level measurements at the monitoring wells were made by use of an electric tape calibrated to 0.01 ft. The staff gage also was calibrated to 0.01 ft. The elevations of the measuring point of the wells and staff gage were surveyed to an accuracy of 0.01 ft as part of a previous site investigation (Roy F. Weston, Inc., 2007).

Bulk Chemical Characteristics of Fill Materials and Stream Sediments

Bulk chemical analyses of fill samples in the slag pile and samples of the stream sediments (Nadine Piatak, U.S. Geological Survey, written commun., 2008) contain high concentrations of iron and aluminum, and smaller amounts of calcium, magnesium, sodium, potassium, and sulfur (table 2 at back of report). More than 100 mg/kg of barium, cerium, cobalt, chromium, gallium, lithium, lead, rubidium, strontium, and vanadium, as well as more than 1,000 mg/kg of copper, manganese, phosphorous, and zinc were detected in at least one sample. Mineralogical analysis provided further insight into the chemistry of the fill material and stream sediments.

Fill Materials

Mineralogical and chemical analyses of nine samples of fill material from the surface of the slag pile indicate that the fill is composed of a variety of mineral types (Nadine Piatak, U.S. Geological Survey, written commun., 2007, 2008) (table 3). Plagioclase feldspars ($NaAlSi_3O_8$ to $CaAl_2Si_2O_8$) are the primary phases in most of the samples. These feldspars generally are calcium rich, indicating that they are anorthite. Potassium rich alkali feldspar ($NaAlSi_3O_8$ to $KAlSi_3O_8$) also is present. Quartz (SiO_2) and its polymorphs cristobalite and tridymite also were identified. Augite ($(Ca,Mg,Fe)SiO_3$) and ferrosilite ($(Ca,Mg,Fe)(Mg,Fe)Si_2O_6$) constitute as much as 45 percent of some samples. Fayalite (Fe_2SiO_4) was 13 to 16 percent by weight in three samples. Hematite (Fe_2O_3) and goethite ($FeO(OH)$) also are present in several samples and likely are weathering products. Mullite ($Al_6Si_2O_{13}$) constituted up to 41 weight percent of one sample. Mullite typically is an anthropogenically produced refractory material that is often used as a furnace liner in refineries; it also may have been used as an additive in the refining process at the site. Zinc-rich minerals, of as much as 38 weight percent ZnO, and iron-rich minerals, of as much as 52 weight percent FeO and as much as 69 weight percent Fe_2O_3, from the spinel group were present in several samples. Gahnite ($ZnAl_2O_4$) is likely to be the zinc-rich spinel mineral. The iron-rich spinel mineral likely is magnetite (Fe_3O_4). Gypsum ($CaSO_4 \cdot 2H_2O$) was detected in several samples and was observed in the field as a precipitate on the bottom surface of slag material in the slag pile. The sulfide minerals pyrite (FeS_2), pyrrhotite (FeS), sphalerite (ZnS), and bornite (Cu_5FeS_4) were detected in the slag samples at less than 1 weight percent. Sphalerite was the primary mineral in the ore that was refined at the site.

Except for zinc in the spinel minerals, manganese, chromium, barium, titanium, zinc, cadmium, and lead were not detected at greater than 4 weight percent in most silicate and oxide mineral phases in any slag sample (Nadine Piatak, U.S. Geological Survey, written commun., 2007, 2008). Glass contained as much as 3.8 weight percent BaO and as much as 1.7 weight percent TiO_2. Augite and spinel contained as much as 3.4 and 2.2 weight percent TiO_2, respectively. Alkali feldspars contain as much as 6.1 weight percent BaO.

Stream Sediments

Several minerals were identified and quantified during analysis of two sediment samples from Grape Creek collected near staff gage SW1 (Nadine Piatak, U.S. Geological Survey, written commun., 2007) (table 3). Sediment samples were collected in May 2006 under non-base flow conditions. pH in the creek during this period likely was somewhat higher than during the sampling period. Quartz is approximately 65 weight percent of both samples. Muscovite ($KAl_2(AlSi_3O_{10})(F,OH)_2$) constitutes 10 to 15 weight percent. Muscovite is a naturally occurring mineral that often is used as an insulating material and can be formed from the chemical alteration of feldspar minerals. Its origin in these samples, from demolition debris or chemical alteration, was not determined. Plagioclase is about 10 weight percent in both samples. Orthoclase ($KAlSi_3O_8$) was detected at about 5 weight percent. Jarosite ($KFe^{3+}_3(OH)_6(SO_4)_2$) was detected at 5 percent by weight in one sample. Jarosite is often produced as a byproduct of zinc refining and also can be formed by the oxidation of iron sulfide minerals in acid drainage environments (Nordstrom, 1982). Goethite was present at 6 percent by weight in one sample. Small amounts of clinochlore ($(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$), and rutile ($TiO_2$), also were detected.

Table 3. Mineralogy of slag and stream-sediment samples at the Hegeler Zinc Superfund site, near Hegeler, Illinois (from Nadine Piatak, U.S. Geological Survey, written commun., 2007, 2008).[1]

[ID, identification; –, no data]

	Samples from slag pile											
Mineral	**Quartz (weight percent)**	**Cristobalite (weight percent)**	**Tridymite (weight percent)**	**Plagioclase (weight percent)**	**Augite (weight percent)**	**Ferrosilite (weight percent)**	**Fayalite (weight percent)**	**Hematite (weight percent)**	**Goethite (weight percent)**	**Mullite (weight percent)**	**Spinel Group (weight percent)**	**Gypsum (weight percent)**
Chemical composition	SiO_2	SiO_2	SiO_2	$NaAlSi_3O_8$ to $CaAl_2Si_2O_8$	$(Ca,Mg,Fe,Al)_2Si_2O_6$	$(Fe,Mg)_2Si_2O_6$	Fe_2SiO_4	Fe_2O_3	$FeO(OH)$	$Al_6Si_2O_{13}$	$(Zn, Fe^{2+})(Fe^{3+},Al,Si)_2O_4$	$CaSO_4{\cdot}2H_2O$
Sample ID												
IL-HG-1	7	2	-	22	-	-	-	36	-	11	-	22
IL-HG-3	2	-	-	37	-	45	-	-	-	-	16	-
IL-HG-5	50	2	-	7	-	-	-	20	4	12	6	-
IL-HG-9A	-	-	-	79	6	-	13	-	-	-	2	1
IL-HG-9B	32	4	10	-	-	-	-	-	-	41	13	-
IL-HG-9C	-	-	-	69	31	-	-	-	-	-	-	-
IL-HG-9D	-	-	-	77	20	-	-	-	1	-	-	3
IL-HG-10	-	-	-	73	9	-	16	-	1	-	-	1
IL-HG-11	1	-	-	76	7	-	14	-	1	-	2	-

	Samples from sediments in Grape Creek							
Mineral	**Quartz (weight percent)**	**Muscovite**	**Plagioclase (weight percent)**	**Orthoclase (weight percent)**	**Jarosite (weight percent)**	**Goethite (weight percent)**	**Clinochlore (weight percent)**	**Rutile (weight percent)**
Chemical composition	SiO_2	$KAl_2(AlSi_3O_{10})(F,OH)_2$	$NaAlSi_3O_8$ to $CaAl_2Si_2O_8$	$KAlSi_3O_8$	$KFe^{3+}_3(OH)_6(SO_4)_2$	$FeO(OH)$	$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$	TiO_2
Sample ID								
IL-HG-1-SS	63	10	9	6	5	6	-	1
IL-HG-2-SS	66	15	12	5	-	-	3	-

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[1] Estimates based on Rietveld refinement of powder X-ray diffraction patterns.

Diel Sampling of Groundwater and Surface-Water Quality

For the purposes of this report, constituents that exhibited a diel variation met two conditions. First, the total range of variation over a 12-hour period was at least 50 percent of the mean value. Second, the timing of the pattern exhibited by the variation over the second 24-hour period was consistent with the timing of the pattern of the first 24-hour period. Many constituents in Grape Creek, such as arsenic, beryllium, lithium, and nickel, fit the first condition. However, the variations in the concentrations of these constituents are relatively random and do not recognizably repeat from one day to the next. Temperature and pH have specific, identifiable diel cycles, but the ranges, as percent of mean, were not computed. Specific conductance also had a smooth, recognizable diel pattern that was consistent from day to day, but its range was less than 50 percent of the mean. These three constituents, temperature, pH, and specific conductance, are the exceptions to the two conditions defined above as necessary for determining a diel cycle, primarily because the diel pattern identified in the other constituents resulted, either directly or indirectly, from the diel changes in these three factors. DO also is important in determining the diel cycles of many minor and trace elements in water, but it satisfies both conditions of range greater than 50 percent and consistent 24-hour patterns; however, it is, itself, dependent upon solar radiation (driving photosynthesis and respiration) and temperature. Finally, uranium is considered to have a diel cycle, even though the mean could not be computed because a large portion of uranium results are below the reporting level.

Analysis of Quality-Assurance and Quality-Control Data

Examination of the laboratory QA/QC data, including laboratory matrix spikes and matrix spike duplicates, and of the field QA/QC data collected at well MW3 and Grape Creek indicates that the laboratory-reported concentrations of the constituents in these samples are accurate (Gary Cotrell, U.S. Geological Survey, written commun., 2008). However, for the purposes of this investigation, accuracy (the agreement between the laboratory-reported concentration and the true concentration) alone is not sufficient. High precision and low bias also are needed. Precision (the degree of agreement between measurements) is determined by the agreement between the results of a sample and its field duplicate. Bias (systematic error introduced during sampling, handling, or analysis) is determined through the analyses of equipment blanks and examination of electroneutrality in the analytical data.

Analytical results for investigative samples and their corresponding field duplicates, which were sequential duplicates in all cases, were pooled for MW3 and Grape Creek. This pooling yielded a set of nine duplicate pairs from which relative standard deviation (as percent; also called coefficient of variation) and mean standard deviations (Mueller and Titus, 2005) were computed for the dataset (table 4). For most constituents, the relative standard deviation is used to determine the adequacy of the sampling results because the reported concentrations are large in comparison to the minimum reported concentration of the constituent. For arsenic, lead, selenium, and vanadium, the mean standard deviation is used because the measured concentrations are within a factor of 10 of the minimum reported concentration of the constituent.

In addition to their utility in assessing the precision of individual sample constituent concentrations, these statistics are needed to help define the conditions for determining if a constituent meets the definition of having a diel cycle. Most mean standard deviations and percent standard deviations are relatively small compared to the range of the respective concentrations. The lower limit for defining diel variations is chosen as 50 percent of the mean concentration. All relative standard deviations are much less than 50 percent. The relative standard deviations or mean standard deviations are also used to determine the 90-percent confidence intervals for the sample concentrations. Table 4 lists the summary of water-quality data from well samples and relative standard deviations or mean standard deviations for constituents.

The data from the equipment blank sample indicate that the sampling techniques introduced no bias into the analyses. Nitrate and nitrite as nitrogen (estimated concentration of 0.034 mg/L), chloride (0.31 mg/L), barium (estimated concentration of 0.05 µg/L), chromium (0.10 µg/L), and zinc (estimated concentration of 0.4 µg/L) were the only constituents detected in the equipment blank. The concentrations of barium, chromium, zinc, and chloride in the equipment blank typically were at least an order of magnitude (and always at least of factor of four) below the minimum concentration in the investigative samples; therefore, the bias in these constituents (as well as in the constituents that were not detected in the equipment blank) is negligible and is not considered further. Nitrate plus nitrite as nitrogen (hereafter referred to as nitrate) was detected in the equipment blank at a concentration about a factor of two lower than the detection limit for the investigative samples. Nitrate was not detected in any of the investigative samples (appendixes 1, 2), so its detection in the equipment blank did not affect the interpretation of the sample results and is not considered further.

Table 4. Summary of water-quality data from well MW3, summary statistics, and relative standard deviations or mean standard deviations for constituents sampled at the Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007.

[mg/L, milligram per liter; µg/L, micrograms per liter; –, not applicable; nd, not determined; <, less than, number is value of reporting level; e, estimated concentration]

Constituent and units	Reporting level, this study	Minimum	Maximum	Arithmetic mean	Arithmetic mean for shallow groundwater in central Illinois[a]	Average standard deviation[b]	Relative standard deviation, in percent[c]	Diel variation observed?	Approximate time of diel maximum value	Approximate time of diel minimum value
Calcium (mg/L)	0.02	490	560	520	97	–	2.2	No	–	–
Magnesium (mg/L)	.014	28	32	30	44	–	2.3	No	–	–
Potassium (mg/L)	.04	4.3	4.9	4.6	2.3	–	2.7	No	–	–
Sodium (mg/L)	.02	36	41	38	21	–	2.3	No	–	–
Sulfate (mg/L)	.18	2,000	2,100	2,050	97	–	1.7	No	–	–
Chloride (mg/L)	.12	3.6	5.8	4.2	9.9	–	5.2	No	–	–
Alkalinity (mg/L as CaCO3)	–	–	–	–	–	–	–	No	–	–
Silica (mg/L)	.02	100	120	110	14	–	2.8	No	–	–
Aluminum (µg/L)	1.6	82,000	96,300	89,200	4.1	–	2.7	No	–	–
Antimony (µg/L)	.06	<.12	.54	nd	nd	–	nd	No	–	–
Arsenic (µg/L)	.12	.80	1.30	1.1	2	0.52	–	No	–	–
Barium (µg/L)	.08	4	6	5.3	180	–	8.8	No	–	–
Beryllium (µg/L)	.06	7.6	20	11	<.008	–	13	No	–	–
Boron (µg/L)	8	3,600	4,300	3,900	28	–	2.4	No	–	–
Cadmium (µg/L)	.04	58	77	67	<.04	–	5.7	No	–	–
Chromium (µg/L)	.12	1.7	2.6	2.3	4.2	–	5.8	No	–	–
Cobalt (µg/L)	.04	24	30	26	1.7	–	4.5	No	–	–
Copper (µg/L)	.4	11	17	14	4.5	–	4.9	No	–	–
Iron (µg/L)	6	10,700	13,700	11,300	1,130	–	[d]2.9	No	–	–
Lead (µg/L)	.12	1	1.8	1.2	<.08	.19	–	No	–	–
Lithium (µg/L)	.6	120	780	370	4	–	12	No	–	–
Manganese (µg/L)	.2	2,600	3,700	3,100	140	–	6.6	No	–	–
Molybdenum (µg/L)	.12	<.12	<.20	nd	nd	–	nd	No	–	–
Nickel (µg/L)	.06	93	120	100	3	–	6.6	No	–	–
Selenium (µg/L)	.08	.44	.84	.58	.76	.14	–	No	–	–
Silver (µg/L)	.1	<.2	<1	nd	nd	–	nd	No	–	–
Strontium (µg/L)	.4	750	1,150	960	<.8	–	6.2	No	–	–

Table 4. Summary of water-quality data from well MW3, summary statistics, and relative standard deviations or mean standard deviations for constituents sampled at the Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. —Continued

[mg/L, milligram per liter; µg/L, micrograms per liter; –, not applicable; nd, not determined; <, less than, number is value of reporting level; e, estimated concentration]

Constituent and units	Reporting level, this study	Minimum	Maximum	Arithmetic mean	Arithmetic mean for shallow groundwater in central Illinois[a]	Average standard deviation[b]	Relative standard deviation, in percent[c]	Diel variation observed?	Approximate time of diel maximum value	Approximate time of diel minimum value
Thallium (µg/L)	0.04	<0.08	e0.4	nd	nd	–	nd	No	–	–
Uranium (µg/L)	.04	2.8	3.9	3.3	1.5	–	3.6	No	–	–
Vanadium (µg/L)	.04	<.1	.34	.13	<.04	0.33	–	No	–	–
Zinc (µg/L)	.6	39,500	46,800	43,100	13	–	2.3	No	–	–
Nitrite + nitrate, as nitrogen (µg/L)	.06	<.06	<.06	nd	nd	–	nd	No	–	–
Nitrite, as nitrogen (µg/L)	.002	e.001	<.002	nd	nd	–	nd	No	–	–
Temperature (degrees Celsius)	–	15.4	16.7	15.8	nd	–	nd	Yes[e]	1400–1600 hours	2200–0500 hours
Dissolved oxygen (mg/L)	nd	.79	3.6	1.2	nd	–	nd	No	–	–
pH (standard units)	–	3.61	4.22	–	–	–	nd	Yes[e]	1100–1600 hours	2200–0600 hours
Specific conductance (microsiemens per centimeter)	nd	2,750	2,780	2,770	nd	–	nd	No	–	–
Oxidation-reduction potential (millivolts)	–	340	380	370	nd	–	nd	No	–	–

[a] Terri L. Arnold, U.S. Geological Survey, written commun., 2007.

[b] Average standard deviation computed from duplicates and only for constituents detected within an order of magnitude of the respective reporting level.

[c] Relative standard deviation computed from duplicates for constituents detected more than an order of mganitude above the respective reporting level.

[d] All computations of relative standard deviation or average standard deviation were based on pooled groundwater and Grape Creek duplicates, except iron. Groundwater duplicates for iron were separated from Grape Creek duplicates.

[e] Apparent diel variation in temperature and pH may be artifact of sampling process.

The charge balances indicate a surplus of anions in every sample. This surplus ranges from -6 to -16 percent (mean of -11 percent) for samples from well MW3 and -2 to -32 percent (mean of -16 percent) for samples from Grape Creek. This mismatch indicates either that the assumed valence state of one or more constituents was incorrect, the concentration of one or more cations was underestimated, or the true concentrations of sulfate—which generally were greater than 99 percent of the sum of the anions in the samples—were substantially overestimated. A graph of the relation between charge imbalance and concentrations of sulfate in Grape Creek samples shows an R^2 of 0.81 (fig. 3), indicating that the charge imbalance in Grape Creek likely is owing to overestimation of concentrations of sulfate. There is no similar relation for sulfate and charge balance in the groundwater samples; however, it is assumed that the charge imbalance in samples from well MW3 also is owing to overestimation of the concentration of sulfate.

To correct for the apparent overestimation of concentrations of sulfate in the lab analyses, concentrations of sulfate for the investigative samples were adjusted in PHREEQC to achieve net electrical balance between anions and cations. The reductions in concentrations of sulfate of the Grape Creek samples ranged from 110 to 950 mg/L or 5 to 34 percent of the unadjusted concentrations. For the groundwater samples, the differences in concentrations of sulfate from reported analytical results to those adjusted to attain net charge balance ranged from 140 to 400 mg/L or 6.3 to 17 percent of the unadjusted concentrations. The adjusted concentrations of sulfate are used throughout the report.

Groundwater Quality

Groundwater-quality data obtained from analysis of samples collected from well MW3 are discussed in four categories: field parameters, nitrogen compounds, major ions, and trace elements. Sample results are presented in appendix 1. Computed sample means and relative standard deviations and mean standard deviations based on replicate samples are listed in table 4.

Field Parameters

The temperature of the water samples from well MW3 ranged from 15.4 to 16.7 °C during the sampling period (table 4). Temperature showed diel variations, being highest in the early afternoon (about 1400 to 1700 hours) and lowest during the night and early morning (about 2200 to 0500 hours) (fig. 4). Diel changes in temperature readings are most likely related to warming of water in the flow-through cell during sampling due to interaction with the surface atmosphere. Water temperature readings from well MW3, particularly the higher values measured during the daylight hours, probably are not representative of conditions in the aquifer.

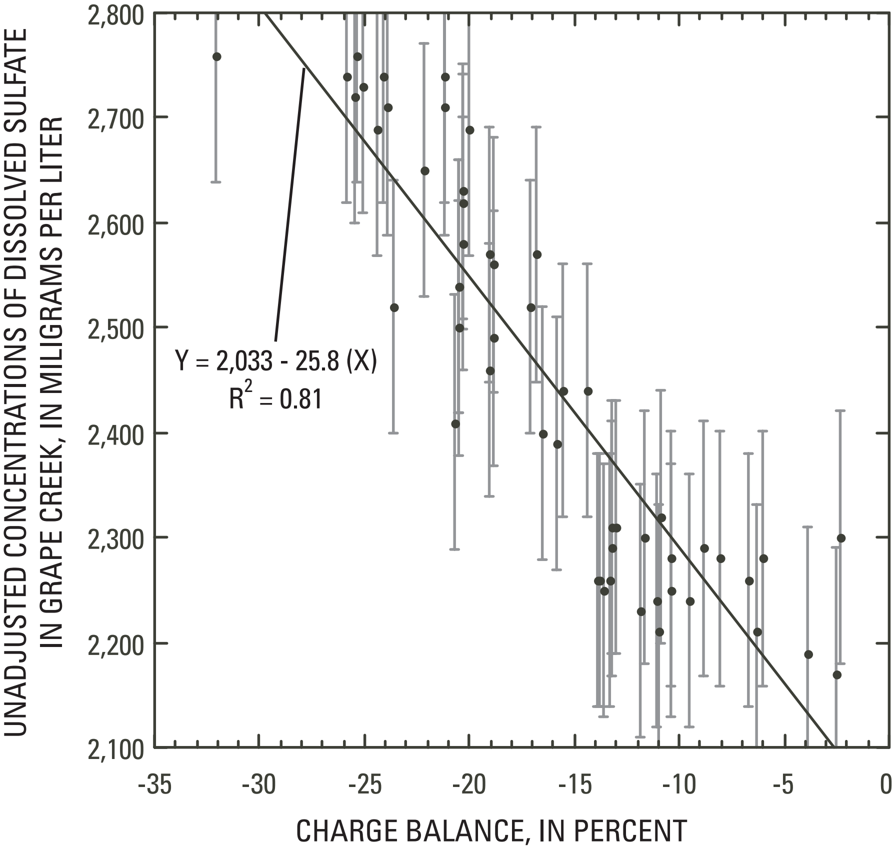

Figure 3. Relation between unadjusted concentrations of dissolved sulfate and cation-anion balance in Grape Creek samples, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007.

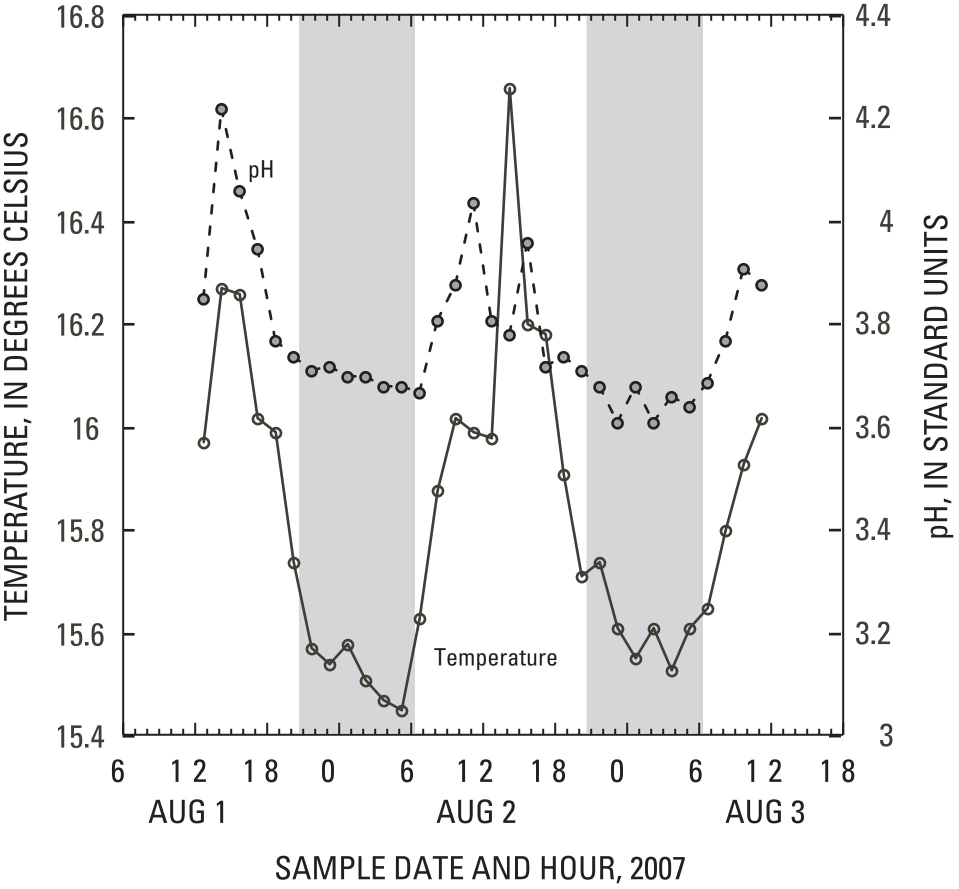

Figure 4. Temperature and pH of water from well MW3, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. (Gray bars indicate night.)

Specific conductance is a result of the combined concentrations of dissolved ions in water. Specific conductance of the water from monitoring well MW3 was essentially constant (2,750 to 2,780 µS/cm; range of less than 1 percent) during the sampling period (table 4), indicating the concentrations of dissolved ions did not vary substantially during the sampling period.

The pH of a solution can affect the aqueous solubility of a number of constituents, particularly metals, thus affecting their concentration and form. The pH of samples from well MW3 ranged from 3.61 to 4.22 (table 4), which is substantially lower than the values of 6–8 typical of uncontaminated shallow groundwater in Illinois. The pH values in samples from well MW3 showed apparent diel variations (fig. 4).

The pH values mirrored temperature, being highest in late morning to early afternoon, and then decreasing until minimum values were measured in the late evening to early morning. The diel variations in the measured pH may be due to the effects of changes in temperature or intensity of solar radiation on pH-affected reactions in the water in the flow-through cell in which the measurements were taken. The pH readings from well MW3, particularly the higher values measured during the daylight hours, probably are not representative of conditions in the aquifer.

The ORP of water is a qualitative indicator of oxidation-reduction conditions in the aqueous environment. The ORP of a solution indicates the potential oxidation state of several chemical constituents, which in turn can affect their form and solubility. The ORP of a solution also affects, and is affected by, the types and activities of the microbiologic communities in an aquifer. ORP values measured in samples from well MW3 showed little variation, ranging from 340 to 380 mV (table 4), indicating stable, moderately oxidizing (electron-donating) conditions in the aquifer.

The concentration of DO in water from well MW3 typically was about 1.0 mg/L during the sampling period (table 4). Concentrations of DO greater than about 0.5 mg/L typically are considered representative of oxic (oxidizing) waters. The presence of DO in the aquifer affects the type and function of microbes that may be active in the aquifer, as well as the potential chemical reactions. Concentrations of DO in well MW3 showed no apparent trends (appendix 1), indicating stable, weakly oxidizing geochemical conditions in the aquifer. However, the concentrations of DO were near the effective lower detection limit of the instrument, so the values are qualitative indicators of the presence of oxygen.

Nitrogen Compounds

The concentration of nitrate in every sample from well MW3 was below the detection limit of 0.06 mg/L (table 4). Nitrite as nitrogen (hereafter referred to as nitrite) was detected in only 4 of the 36 samples collected (sample number includes duplicates) at an estimated concentration of 0.001 mg/L. Nitrite was detected on different days from 0945 through 1715 hours (appendix 1). Nitrite was not detected in the two duplicate samples collected during these four sampling events (appendix 1), indicating that the concentration of nitrite at well MW3 is at concentrations below, but near, 0.001 mg/L. Samples were not analyzed during this investigation for ammonia (concentration of ammonium can be calculated from ammonia concentration and pH), the other nitrogen compounds often present at substantial concentrations in groundwater.

Major Ions

Water samples from well MW3 were analyzed for the major ions–calcium, magnesium, sodium, potassium, chloride, and sulfate (table 4; appendix 1). Calcium, magnesium, sodium, potassium, bicarbonate, chloride, and sulfate are present at high concentrations in most waters because they are among the primary components of most minerals, including those in the fill and glacial drift that are in contact with infiltrating precipitation and groundwater in the vicinity of well MW3. The concentrations of these constituents in water also is affected by the geochemical conditions in the aquifer that affect mineral dissolution and precipitation.

Sample results indicate that calcium is the dominant cation in groundwater beneath the site and that sulfate is the dominant anion (table 4). Concentrations of both calcium and sulfate are substantially elevated in samples from well MW3 relative to their concentrations in typical shallow groundwater in central Illinois, indicating that the dissolution of minerals in the fill material is a substantial source of these constituents in site groundwater. Dissolution of calcium- and sulfur-bearing minerals in the fill likely is enhanced by, and in the case of sulfur contributes to, the low pH of the site groundwater.

Concentrations of the remaining major ions in samples from well MW3 were either detected within or at about a factor of two of the concentrations typical of shallow groundwater in central Illinois (potassium, magnesium, sodium) or were substantially lower (alkalinity; table 4). Because of the acidity of this water (pH less than 4.2), its alkalinity was not measured. Bicarbonate ion (HCO_3^-), the primary component of alkalinity and the dominant anion in most Illinois aquifers, is fully protonated (H_2CO_3) at the pH values measured in well MW3 and, thus, is absent from this groundwater. These results indicate that dissolution of carbonate minerals in the fill deposits may not be a substantial source of constituents to groundwater under the site or that additional reactions are occurring that alter the phase of some of these constituents in the groundwater.

With the exception of chloride, concentrations of the major ions varied by less than 15 percent of the arithmetic mean during the sampling period (table 4). Concentrations of chloride varied by 51 percent of the arithmetic mean. These analyses, combined with trend analysis, indicate that the concentrations of the major ions were similar throughout the sampling period and did not exhibit diel variations or any other discernible trends.

Trace Elements

Water samples from well MW3 were analyzed for 24 trace elements (table 4). Concentrations of trace elements are low relative to the major ions in most water samples because trace elements are minor components of most common minerals (the exceptions are silica and aluminum, which are primary components of the aluminosilicate minerals, and iron, which is a primary component of several minerals). In addition, these elements usually are at low concentrations because under typical geochemical conditions, they have low solubility in water.

Antimony, molybdenum, silver, and thallium were detected in a maximum of 20 percent of the samples from well MW3 (table 4) and are not discussed further in this section. Of the 20 remaining trace elements for which samples were tested, vanadium was detected in about 75 percent of the samples, and the remaining trace elements were detected in every sample. Concentrations of lithium in the samples from well MW3 showed a high degree of variation over the course of the sampling period and between successive sampling events. Lithium data are considered to be unreliable and are not discussed further.

Aluminum, boron, iron, manganese, silica, and zinc were the only trace elements whose arithmetic mean concentrations in groundwater exceeded 1 mg/L (table 4). The mean concentrations of these trace elements, along with those of beryllium, cadmium, cobalt, copper, lead, lithium, manganese, nickel, strontium, and, perhaps, vanadium in site groundwater exceed the mean concentrations of these elements in shallow groundwater in central Illinois by at least a factor of three, and typically by more than an order of magnitude (table 4). These results indicate that dissolution of minerals in the fill deposits containing these elements is a substantial source of these constituents in site groundwater. This mineral dissolution likely is substantially enhanced by the low pH of the site groundwater.

None of the trace elements exhibited diel variations in concentration during the sampling period (table 4). However, several trace elements exhibited other trends. Concentrations of copper increased overall from about 11 to about 16 µg/L. Concentrations of cadmium increased overall from about 60 to about 75 µg/L.

Concentrations of arsenic, beryllium, cobalt, manganese, nickel, and strontium showed a complex trend during the sampling period. Concentrations of these constituents typically decreased from the start of the sampling at 1245 through about 1715 on August 1, were similar from about 1715 on August 1 through about 1545 on August 2, increased from 1545 to 1715 on August 2, were similar from 1715 on August 2 through 0045 on August 3, and were variable from about 0215 hours on August 3 through the end of the sampling period at 1115 hours on August 3. Concentration differences typically were less than about 15 µg/L for arsenic, beryllium, cobalt, and nickel, but this variation resulted in a range in concentrations of beryllium of about a factor of two (table 4). Differences in concentration exceeded 200 µg/L for manganese and strontium, but this variation still resulted in a variation that was less than about one-third of the total range in concentration for those constituents. The variation in the concentrations of arsenic, beryllium, cobalt, manganese, nickel, and strontium may be related to differences in the dilution factors for at least some of the analyses.

Concentrations of chemical constituents in samples from well MW3 show a high degree of correlation (R^2 values greater than 0.70) among calcium, magnesium, and sodium (table 5 at back of report). A high degree of correlation also exists between concentrations of cadmium and uranium. A high to moderate degree of correlation (R^2 values greater than 0.50 but less than 0.71) was observed among calcium, magnesium, sodium, and silica; boron, zinc, and aluminum; and manganese, beryllium, cobalt, and nickel. These correlations may indicate that similar chemical processes are affecting these constituents. The correlation between manganese, beryllium, cobalt, and nickel also may reflect trends in concentration resulting from differences in the dilution factors of these samples. Samples with higher laboratory dilution factors tended to have higher reported concentrations than samples from the same wells that had lower laboratory dilution factors.

Geochemical Modeling

The species distribution and mineral saturation indices for the samples from well MW3 were computed in PHREEQC by use of pH (3.68) and temperature (15.5 ^{o}C) values measured from about 2 to 4 AM CDT. These values were chosen because they were probably the most representative of conditions in the groundwater.

Results of geochemical modeling of the sample data collected from well MW3 were compared to the mineralogy of the slag (table 3) as well as to the likely mineralogy of the other fill materials and glacial deposits beneath the site (table 6 at back of report). Modeling results indicate this water is undersaturated with respect to most of the minerals considered (negative saturation index) and that there is the potential for dissolution of the primary end-member minerals of the plagioclase series (albite, anorthite); spinel group (gahnite, hercynite, magnetite); pyroxene group (including augite); the sulfide minerals pyrite, sphalerite, and chalcopyrite; and some of the iron hydroxides. It is likely that dissolution of these minerals, along with residual secondary minerals, is adding dissolved constituents to groundwater. Modeling results also indicate that these samples are supersaturated (positive saturation index greater than +0.1) with respect to the hydrous sulfate minerals alunite ($KAl_3(SO_4)_2(OH)_6$) and jarosite, the iron oxyhydroxide goethite, and the iron oxide hematite. It is possible that precipitation of these minerals or related minerals, such as schwertmannite ($Fe_8O_8(OH)_6SO_4$; Bigham and others, 1996), is limiting the maximum concentration of iron and aluminum in groundwater. Finally, the model results indicate that this water is at or near saturation for gypsum, so that changes in the concentration of sulfate or calcium in the aquifer may be limited by the precipitation and dissolution of this mineral.

It is noted that the thermochemical constants in the PHREEQC model are based on minerals with simple, ideal, chemical compositions. Because the chemical compositions of actual minerals (including those at the site) tend to be a complex mixture of elements in varying proportions, the true saturation indices of the site minerals may vary substantially from the results indicated by PHREEQC.

Discussion

Water-quality data collected from well MW3 indicates stable, low pH, weakly oxidizing conditions in the aquifer during the sampling period. These conditions resulted in constituent concentrations that generally showed little variation through time and no diel variations in the aquifer. The absence of diel variations in the concentrations of groundwater constituents indicate that groundwater samples can be collected at any time without affecting the results, with the exception of pH and temperature, which appear to be influenced by ambient atmospheric conditions.

Water-quality data, mineral data, and geochemical modeling indicate that the low pH of water in well MW3, as well as the high concentrations of iron and sulfate, likely are the result of the oxidation of iron sulfide minerals such as pyrite in the fill. These reactions consume oxygen

$$FeS_2 + (15/4)O_2 + 7/2H_2O \Leftrightarrow Fe(OH)_3 + 2SO_4^{-2} + 4H^+ \qquad (6)$$

as well as ferric iron (Fe^{3+}) as the water becomes more acidic,

$$FeS_2 + 14Fe^{3+} + 8H_2O \Leftrightarrow 15Fe^{2+} + 2SO_4^{-2} + 16H^+ \text{ (Nordstrom, 1982).} \qquad (7)$$

The low pH in the groundwater near well MW3 likely has enhanced the dissolution of other classes of minerals (primarily carbonates and aluminosilicates) in contact with soil water and groundwater. This enhanced mineral dissolution accounts for the high concentrations of calcium, aluminum, beryllium, boron, cadmium, cobalt, lead, manganese, nickel, silica, strontium, and zinc in groundwater at the site relative to typical shallow groundwater in central Illinois (table 4). Dissolution of the carbonate minerals that typically are in soils and aquifer materials in central Illinois would tend to consume hydrogen ions and raise the pH of the groundwater. The presence of low pH groundwater beneath the site indicates that sulfide mineral oxidation was occurring at a higher rate in the aquifer and fill material than the dissolution of carbonate minerals during the sampling period. Carbonate minerals may have been partly or completely leached from the shallow subsurface at the site by the low-pH waters.

Water-quality data, mineralogy, and geochemical modeling indicate that the high concentrations of zinc at well MW3 may be largely derived from dissolution of sphalerite and gahnite. The correlation between zinc and aluminum (table 6) indicates that dissolution of gahnite may be a substantial source of zinc in the site groundwater.

Correlations among constituents (table 5), mineralogy, and geochemical modeling indicate that the concentrations of calcium, magnesium, sodium, and silica may be derived partly or completely from the dissolution of calcium-, magnesium-, and sodium-containing silicate minerals. These minerals may include anorthite, albite, and augite.

Because beryllium, boron, cadmium, cobalt, lead, manganese, nickel, and strontium either were not included in the analyses of the slag, were not detected, or were detected at concentrations of less than 1 weight percent, water-quality data and geochemical modeling did not clearly indicate specific sources of the high concentrations (relative to ambient shallow groundwater) of these elements in the groundwater from well MW3. Geochemical modeling indicates that the water samples from well MW3 were unsaturated with respect to all of the identified minerals in which these constituents occur as primary constituents. Dissolution of minerals is possible in the slag and other fill materials (coal ash, mine spoil), as well as in the underlying glacial deposits in which these elements are major constituents. However, these elements are probable trace constituents in the minerals identified in the slag and in the minerals that are likely to be in the glacial deposits and other components of the fill. Their presence in the groundwater also may be due to dissolution of minerals in which they are secondary or trace constituents. For example, cadmium is often associated with sphalerite (*http://minerals.usgs.gov/minerals/pubs/commodity/cadmium/*) and was recovered as a byproduct of the zinc smelting at the Hegeler site. A gaseous form of boron is used in the smelting of zinc, but boron can leach from coal ash (Buszka and others, 2007), one of the fill materials at this site.

Surface-Water Quality

Surface-water-quality data obtained from analysis of samples collected from Grape Creek are divided into field measurements, nitrogen compounds, major ions, and trace elements. Sample results are presented in appendix 2. Computed means for samples and relative standard deviations and mean standard deviations based on replicate samples are listed in table 7.

Field Parameters

Water temperature in Grape Creek ranged from 20.9 to 27.3 °C during the sampling period (table 7). Temperature varied on a diel basis, being highest from about 1545 to 1830 hours and lowest from about 0630 to 0800 hours (fig. 5*A*).

Specific conductance in Grape Creek ranged from about 2,500 to 2,970 µS/cm during the sampling period (table 7). Specific conductance varied on a diel basis with a range of 17 percent (fig. 5*B*). However, the variation in specific conductance was never greater than 10 percent of the mean value. Specific conductance typically was highest from about 1500 to 1900 hours and lowest from about 2200 to 0500 hours.

The pH of Grape Creek ranged from 3.03 to 3.47 during the sampling period (fig. 5*C*). Although the trends were complex, pH values appeared to show diel variation. The pH values in the creek were at or near their daily minimum during the late afternoon and early evening hours from about 1600 to 2100. The pH values were highest during the late evening and early morning hours until about 0900, and then they decreased during the rest of the morning and the early afternoon.

ORP values in Grape Creek ranged from 410 to 540 mV during the sampling period (fig. 5*D*). ORP was characterized by several hours of generally increasing values followed by large decreases over periods of 1 to 4 hours. Whether ORP was related to a specific redox reaction in the creek is not known, but it is considered to be unlikely. ORP values here are considered as a qualitative indicator of geochemical conditions.

The concentration of DO in Grape Creek varied by more than an order of magnitude during the sampling period, ranging from 0.54 to 6.0 mg/L (table 7). Concentrations of DO varied on a diel basis, and were lowest (typically less than 0.80 mg/L) between about 0500 and 1130 and highest between about 1330 and 1630 on a given day (fig. 5*E*).

Nitrogen Compounds

The concentration of nitrate in every sample from Grape Creek was below the detection limit of 0.06 mg/L (table 7). Concentrations of nitrite in samples from Grape Creek ranged from below the detection limit of 0.002 mg/L to 0.010 mg/L. Concentrations of nitrite showed a limited range during the sampling period, but had clear diel trends (fig. 6). Nitrite typically was not detected between about 2015 hours and 0915 hours. The maximum daily concentration occurred from about 1115 to 1615 hours. The magnitude of the change in the concentration of nitrite over the diel cycle cannot be precisely determined, but based on the variations in the estimated concentrations, it is about a factor of five.

Table 7. Summary of water-quality data from Grape Creek, summary statistics, and relative standard deviations or mean standard deviations for constituents sampled at the Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007.

[mg/L, milligram per liter; µg/L, micrograms per liter; –, not applicable; nd, not determined, <, less than; e, estimated concentration; gray indicates maximum 12-hour range greater than 50 percent of mean]

Constituent and units	Reporting level, this study	Minimum	Maximum	Arithmetic mean	Maximum as percent of mean	Minimum as percent of mean	Maximum 12-hour range as percent of mean	Average standard deviation	Relative standard deviation, in percent	Diel cyclic pattern[e]	Approximate time of diel maximum value	Approximate time of diel minimum value
Calcium (mg/L)	0.02	440	529	480	110	92	–	nd	2.2	No	–	–
Magnesium (mg/L)	.014	30	37	33	112	91	–	nd	2.3	No	–	–
Potassium (mg/L)	.04	6.7	7.6	7.1	107	94	–	nd	2.7	No	–	–
Sodium (mg/L)	.02	33	40	36	110	92	–	nd	2.3	No	–	–
Sulfate (mg/L)	.18	1,800	2,200	2,000	113	90	20	nd	1.7	No	–	–
Chloride (mg/L)	.12	4.2	6.7	5.7	117	74	44	nd	5.2	No	–	–
Alkalinity (mg/L as CaCO3)	–	0	0	0	nd	nd	–	nd	nd	–	–	–
Silica (mg/L)	.018	60	71	66	107	91	17	nd	2.0	No	–	–
Aluminum (µg/L)	1.6	40,200	51,600	47,100	110	85	24	nd	2.7	No	–	–
Antimony (µg/L)	.06	<.12	<.60	nd	nd	nd	–	nd	nd	No	–	–
Arsenic (µg/L)	.12	2.3	5.3	3.90	136	59	56	0.52	nd	No	–	–
Barium (µg/L)	.08	10	20	15	136	67	60	nd	8.8	Yes	1315 to 1815	2215 to 1015
Beryllium (µg/L)	.06	5.7	19	12	158	48	103	nd	2.6	No	–	–
Boron (µg/L)	8	3,200	3,600	3,400	106	94	12	nd	2.4	No	–	–
Cadmium (µg/L)	.04	18	26	21	123	86	38	nd	.7	No	–	–
Chromium (µg/L)	.12	<.5	.8	[a].56	nd	nd	–	nd	nd	No	–	–
Cobalt (µg/L)	.04	45	70	57	122	79	44	nd	4.5	No	–	–
Copper (µg/L)	.4	<1.0	10	[a]2.3	nd	nd	–	nd	nd	No	–	–
Iron (µg/L)	6	33,600	168,000	128,000	131	26	63	nd	2.0	Yes	2315 to 0615	1315 to 1615
Lead (µg/L)	.12	1.6	3.7	2.6	142	62	68	.19	nd	Yes	1115 to 1415	2015 to 0515
Lithium (µg/L)	.6	140	780	540	144	26	69	nd	12	No	–	–
Manganese (µg/L)	.2	2,800	4,600	3,650	125	77	42	nd	6.6	No	–	–
Molybdenum (µg/L)	.12	<.2	1.2	nd	nd	nd	–	nd	nd	No	–	–
Nickel (µg/L)	.06	230	410	300	136	77	59	nd	6.6	No	–	–
Selenium (µg/L)	.08	.4	1.1	.72	153	56	83	.14	nd	No	–	–
Silver (µg/L)	.1	<.2	<1	nd	nd	nd	–	nd	nd	No	–	–
Strontium (µg/L)	.4	430	840	590	143	73	69	nd	6.2	No	–	–

Table 7. Summary of water-quality data from Grape Creek, summary statistics, and relative standard deviations or mean standard deviations for constituents sampled at the Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. —Continued

[mg/L, milligram per liter; µg/L, micrograms per liter; –, not applicable; nd, not determined, <, less than; e, estimated concentration; gray indicates maximum 12-hour range greater than 50 percent of mean]

Constituent and units	Reporting level, this study	Minimum	Maximum	Arithmetic mean	Maximum as percent of mean	Minimum as percent of mean	Maximum 12-hour range as percent of mean	Average standard deviation	Relative standard deviation, in percent	Diel cyclic pattern[e]	Approximate time of diel maximum value	Approximate time of diel minimum value
Thallium (µg/L)	0.04	<0.08	[e]0.2	[a]0.17	nd	nd	–	nd	nd	No	–	–
Uranium (µg/L)	.04	<.40	[e].20	nd	nd	nd	–	nd	nd	Yes	1315 to 1915	2015 to 1015
Vanadium (µg/L)	.04	<.1	5.8	[a]3.9	nd	nd	64	0.33	nd	Yes	0415 to 0715	1315 to 1415
Zinc (µg/L)	.6	52,500	65,200	60,200	108	87	21	nd	2.3	No	–	–
Nitrite + Nitrate, as Nitrogen (µg/L)	.06	<.06	<.06	nd	nd	nd	–	nd	nd	No	–	–
Nitrite, as Nitrogen (µg/L)	.002	<.002	.010	nd	nd	nd	–	nd	nd	Yes	1115 to 1615	2015 to 0915
Temperature (degrees Celsius)	–	20.9	27.3	24.1	113	87	–	nd	nd	Yes	1545 to 1830	0630 to 0800
Dissolved oxygen (mg/L)	–	.54	6	2.5	–	–	183	nd	nd	Yes	1330 and 1630	0500 to 1130
pH (standard units)	–	3.03	3.47	–	–	–	–	nd	nd	Yes	2200 to 0800	1900
Specific conductance (microsiemens per centimeter)	nd	2,500	2,970	2,730	109	92	17	nd	nd	Yes	1500 to 1900	2200 to 0500
Oxidation-reduction potential (millivolts)	–	410	540	450	120	91	29	nd	nd	Uncertain	–	–

[a] Mean calculated by the Kaplan–Meier method (Helsel, 2005).

[b] Average standard deviation computed from duplicates and only for constituents detected within an order of magnitude of the respective reporting level.

[c] Relative standard deviation computed from duplicates for constituents detected more than an order of mganitude above the respective reporting level.

[d] All computations of relative standard deviation or average standard deviation were based on pooled groundwater and Grape Creek duplicates, except iron. Groundwater duplicates for iron were separated from Grape Creek duplicates.

[e] For this report, diel cyclic pattern is defined as a maximum 12-hour variation of more than about 50 perecnt of the mean and the pattern was consistent from day one to day two of data collection.

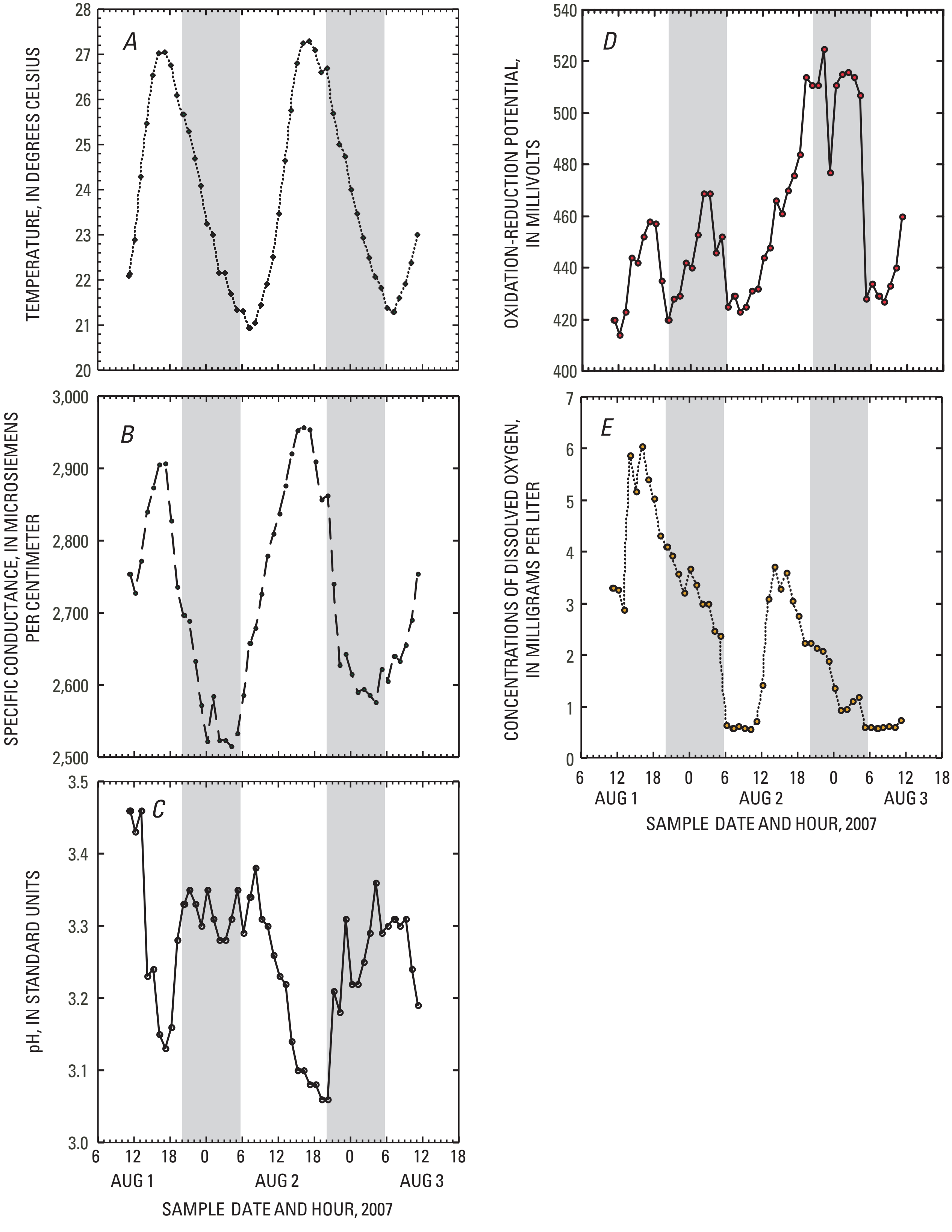

Figure 5. Graph through time of (*A*) temperature, (*B*) specific conductance (*C*) pH, (*D*) oxidation-reduction potential, and (*E*) concentrations of dissolved oxygen in Grape Creek, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. (Gray bars indicate night. Oxidation-reduction potential is voltage measured in the water using a saturated calomel or similar electrode.)

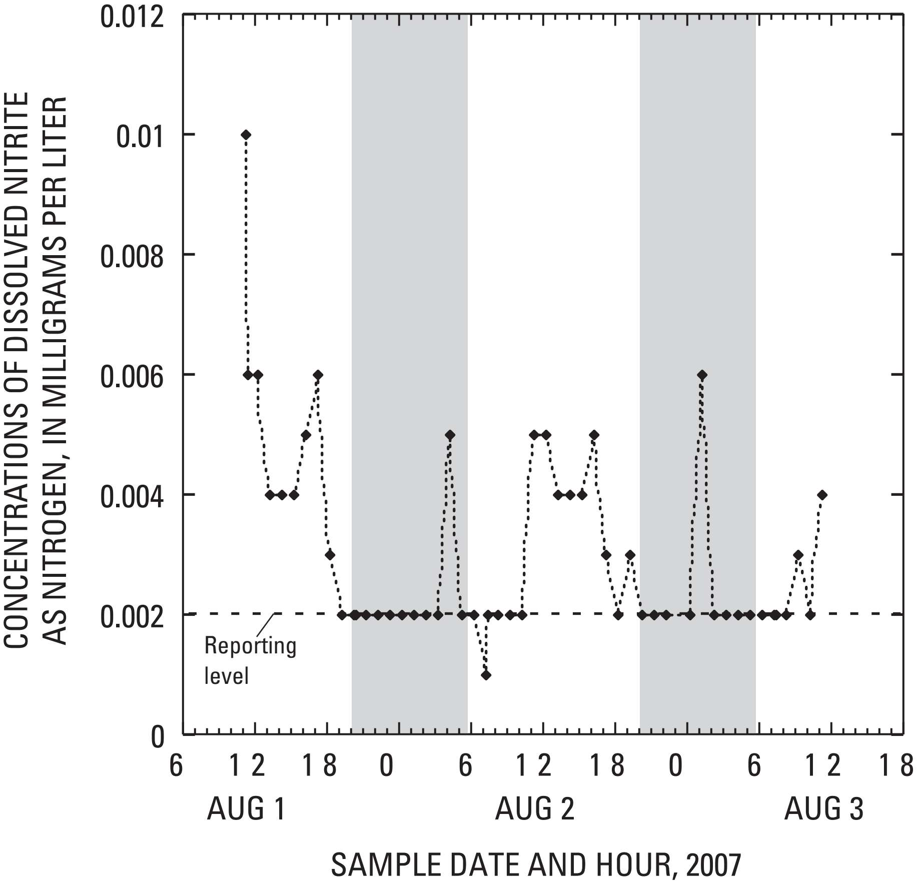

Figure 6. Concentration of nitrite as nitrogen in Grape Creek, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. (Gray bars indicate night. Dashed line indicates U.S. Geological Survey National Water-Quality Laboratory reporting level for nitrite as nitrogen concentration.)

Major Ions

Similar to groundwater, calcium is the dominant cation in Grape Creek and sulfate is the dominant anion (table 7). Because of the acidity of this water (pH less than 4.2), its alkalinity could not be measured. Bicarbonate ion (HCO_3^-), the primary component of alkalinity and the dominant anion in most Illinois surface water, is fully protonated (H_2CO_3) at the pH values measured at staff gage SW1, and, thus, is absent from this reach of Grape Creek.

Concentrations of calcium, magnesium, sodium, and potassium varied by less than 20 percent of the arithmetic mean during the sampling period (table 7). Concentrations of sulfate varied by about 25 percent of the arithmetic mean, and concentrations of chloride varied by about 40 percent. Concentrations of calcium (fig. 7), chloride, magnesium, and sodium appear to show a small overall decrease during the sampling period, but diel variations in concentration were not observed for any of the major ions.

Trace Elements

Water samples from Grape Creek were analyzed for 24 trace elements (appendix 2; table 7). As was the case in samples from well MW3, aluminum (fig. 7), boron, iron, manganese, silica, and zinc (fig. 7) were the only trace elements whose arithmetic mean concentration in samples from Grape Creek exceeded 1 mg/L. As was also the case in samples from well MW3, antimony, molybdenum, and silver were not detected in most or all of the samples from Grape Creek and are not discussed further. Concentrations of lithium in the samples from Grape Creek showed a high degree of variation over the course of the sampling period and between successive sampling events. Lithium data are considered to be unreliable and are not discussed further. Select samples also were analyzed for mercury, which was not detected in any sample at a detection limit of 0.01 µg/L; therefore, mercury is not discussed further.

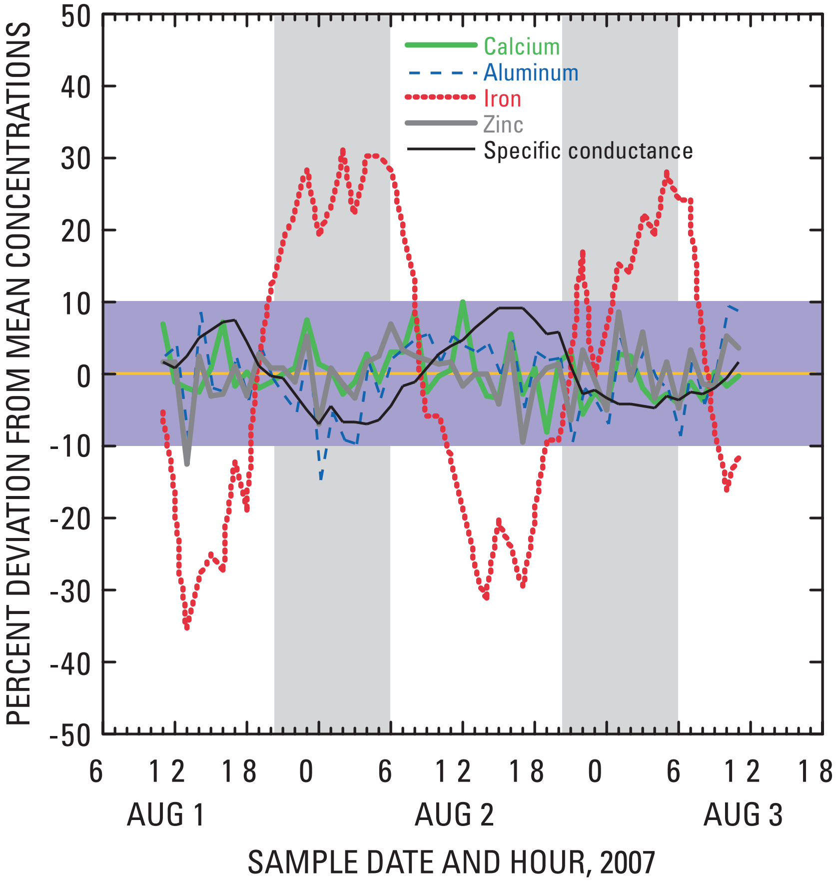

Figure 7. Percent deviation of concentrations from the mean of calcium, aluminum, iron, zinc, and specific conductance in Grape Creek, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. (Gray vertical bars indicate night and the violet horizontal bar indicates 20-percent range of deviation from the mean.)

Concentrations of aluminum, arsenic, boron, cadmium, chromium, selenium, silica, thallium, and zinc in Grape Creek showed little variation through time during the sampling period, either in absolute terms or as a percentage of the total concentration. The concentrations of these constituents appear to be unaffected by any diel variations in geochemistry in Grape Creek during the sampling period. Concentrations of beryllium and cobalt in Grape Creek showed no discernible trends through time during the sampling period, but they exhibited substantial variation between some successive sampling events. The variation in the concentrations of these constituents appears to be partly related to dilution factor during laboratory processing.

Concentrations of copper, manganese, nickel, and strontium showed some tendency to exhibit highest and lowest concentrations during certain parts of one day, but these patterns either were not repeated on both days of the sampling period, or the magnitude of the change was too small in relation to the overall variation in concentrations to clearly indicate a diel cycle. The variation in the concentrations of manganese, nickel, and strontium appears to be partly related to the laboratory dilution of the samples. However, the variation in the concentrations of copper bears no obvious relation to dilution factor or other laboratory artifacts and appears to represent conditions in Grape Creek.

Identification of diel variations is highlighted by plotting normalized concentrations (the sample concentration divided by the mean concentration of the specific constituent in all samples) of calcium, aluminum, iron, and zinc (fig. 7). Specific conductance is also shown normalized to its mean. Concentrations of aluminum, calcium, and zinc vary by less than 10 percent about the mean and show no consistent temporal trends. Iron, however, exhibits normalized concentrations that vary by more than 30 percent above or below the mean and during consistent times of the day, indicating clear diel variations in concentration.

The normalized concentrations of barium, lead, and vanadium (fig. 8) and actual concentrations of uranium (fig. 9) also exhibited clear or (in the case of uranium) likely diel variations during the sampling period (table 7). Trends in the concentrations of these constituents are not substantially affected by differences in date of laboratory analysis, sample dilution factor (with the exception of uranium), or other variations in the precision of the laboratory instruments. The variation in concentration through time for these constituents appears to be indicative of the conditions in Grape Creek.

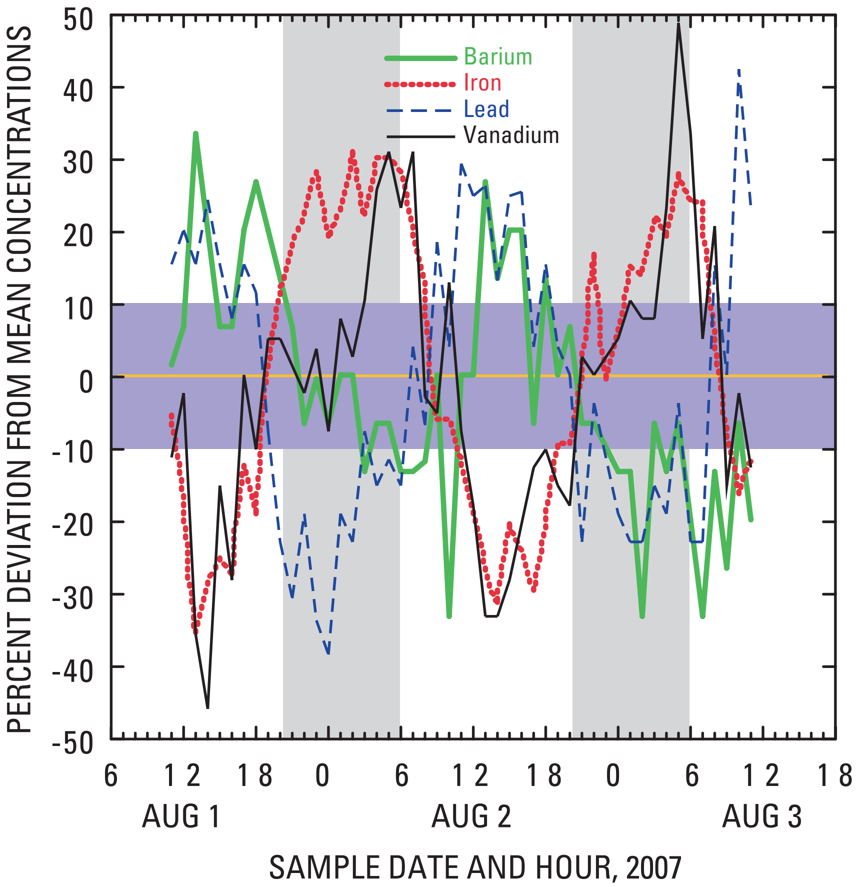

Figure 8. Percent deviation of concentrations from the mean of barium, iron, lead, and vanadium in Grape Creek, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. (Gray vertical bars indicate night and the violet horizontal bar indicates 20-percent range of deviation from the mean.)

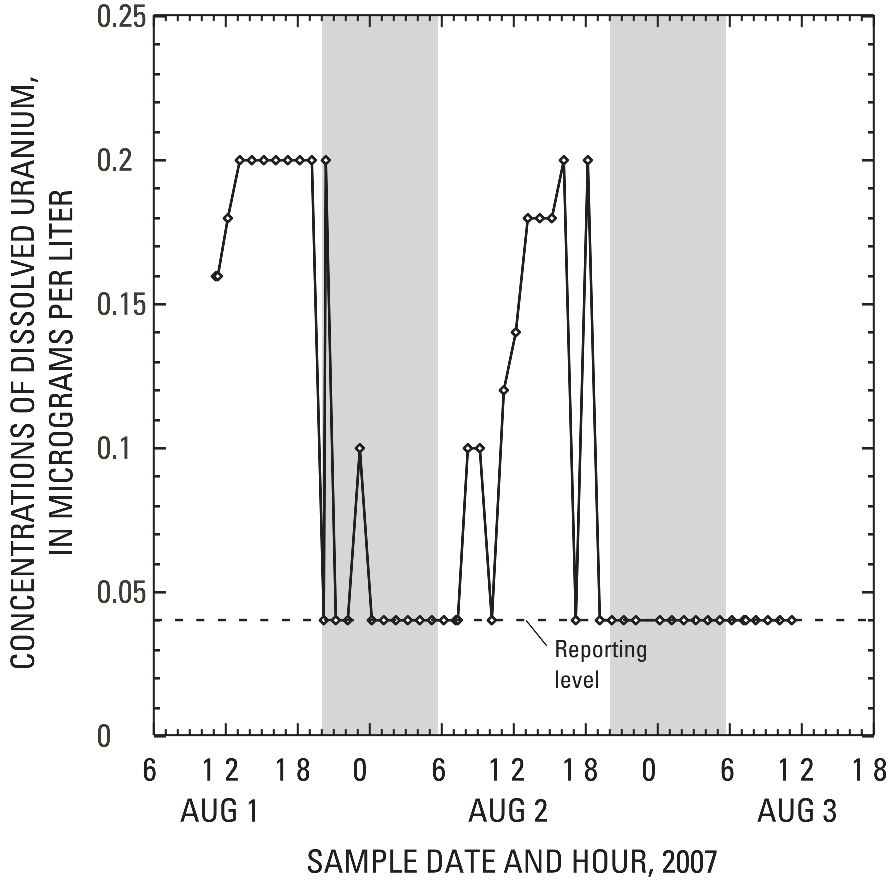

Figure 9. Concentration of dissolved uranium in Grape Creek, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. (Gray bars indicate night. Dashed line indicates U.S. Geological Survey National Water-Quality Laboratory reporting level for uranium concentration.

Concentrations of barium were somewhat variable between successive sampling events, obscuring the diel variations (fig. 8). However, the highest concentrations of barium were consistently detected from about 1315 through about 1815 hours, and the lowest concentrations were consistently detected from about 2215 hours through about 1015 hours. The magnitude of the diel variations was about 5 to 6 µg/L, about one-third of the total concentration.

Concentrations of iron exhibited generally consistent trends of small increases and decreases between successive sampling events that combine to show clear diel variations during the sampling period (fig. 8). Trends in concentrations of iron varied somewhat between days, but concentrations typically were lowest during the early- to mid-afternoon (about 1315 hours to about 1615 hours) and highest during the late evening through midmorning hours (about 2315 to 0615 hours). Concentrations of iron differed by about a factor of two during the diel cycle.

Concentrations of lead also exhibited generally consistent trends of small increases and decreases between successive sampling events that combine to show clear diel variations during the sampling period (fig. 8). The timing of the concentration trends differed somewhat between days, but concentrations of lead typically were lowest from late evening to early morning (about 2015 hours to about 0515 hours) and typically were highest during the late morning and early afternoon (about 1115 to 1415 hours). Concentrations of lead differed by about a factor of two during the diel cycle.

Identification of potential trends in concentrations of uranium is limited by the high percentage of nondetections (related to higher dilution factors) and by the fact that most of the detections are estimated values (appendix 2, fig. 9). However, concentrations of uranium typically were below the reporting level from about 2015 to 1015 hours and typically were highest from about 1315 to 1915 hours during the sampling period, indicating that diel variations of concentrations of uranium occur in the creek. The magnitude of the change in the concentration of uranium over the diel cycle cannot be precisely determined, but, based on the variations in the estimated concentrations, it is at least a factor of two.

Concentrations of vanadium were variable between successive sampling events, obscuring the diel variations, and they differed somewhat from day to day (fig. 8). However, concentrations of vanadium consistently were lowest at about 1315 to 1415 hours then increased to maximum concentrations at about 0415 to 0715 hours before decreasing. Concentrations of vanadium differed by more than a factor of two during the diel cycle.

Concentrations of chemical constituents in samples from Grape Creek show a high ($R^2 > 0.7$) degree of correlation among magnesium, potassium, and sodium and a moderate ($R^2 > 0.5$ but < 0.7) degree of correlation between calcium, potassium, and sodium (table 8 at back of report). High degrees of correlation also exist between concentrations of manganese and beryllium; manganese and cobalt; iron and vanadium; among cobalt, selenium and strontium; and between the concentration of lead and the intensity of solar radiation. A moderate degree of correlation exists between concentrations of several constituents, including beryllium and cobalt, and between cobalt and cadmium. In addition, a strong inverse relation exists between concentrations of iron and DO, and between iron and the intensity of solar radiation, and a moderate inverse correlation exists between pH and specific conductance.

Geochemical Modeling

Results of PHREEQC modeling of the water-quality data of each sample collected from Grape Creek were compared to the mineralogy of the stream sediments and other minerals likely to affect water quality (table 9 at back of report). Model results indicate that the samples are undersaturated with respect to most of the minerals modeled, including the primary end-member minerals of the plagioclase series (albite, anorthite), K-feldspar (orthoclase), muscovite, and clinochlor. It is possible that dissolution of these minerals is adding their constituents to the creek water.

Model results also indicate that these samples typically are supersaturated with respect to barite, goethite, hematite, and jarosite. The results also indicate that an amorphous iron hydroxide with the formula $Fe(OH)_{3(am)}$ is near saturation but varies over the 24-hour period and its saturation state is dependent on the pH and concentration of iron. It is possible that precipitation of these minerals or a similar metastable phase such as schwertmannite (Bigham and others, 1996; Cravotta, 2008) is removing iron and sulfate from the creek water. Schwertmannite is supersaturated (table 9) but is metastable over a range of conditions in nature, and the results shown in table 9 are considered only qualitative. The modeling indicates that this water is consistently at or near saturation for gypsum, so that changes in the concentration of sulfate or calcium in the aquifer will affect the precipitation or dissolution of this mineral.

The saturation indices of several minerals showed diel trends (table 9). Saturation indices often were lowest for unsaturated minerals (highest for saturated) from about 1515 to 2015 hours and highest at about 0000 to 0600 hours, indicating that the intensity of the precipitation and dissolution for many minerals should be affected by diel variations in temperature and pH. However, the values of the saturation indices for most minerals were positively correlated with the concentrations of their constituents in Grape Creek ($R^2 = 0.63$ for the concentration of barium and the saturation index of barite for example), which is contrary to the high degree of negative correlation that would be expected if constituent concentrations in water were controlled by the intensity of mineral precipitation or dissolution during the sampling period. It appears, therefore, that for many constituents, variations in the value of the saturation indices likely reflect variations in the concentration of the constituent compounds for that mineral in a given sample (as well as variations in temperature and pH) rather than the variations in constituent concentrations in the water sample. The apparent lack of influence of the value of the saturation index for a mineral on its constituent concentrations in water indicates that kinetic effects on mineral precipitation and dissolution may be important. Geochemical modeling indicates that while pH- and temperature-induced variations in the intensity of precipitation and dissolution reactions may affect concentrations of constituents in water, a straightforward cause and effect does not exist between the intensity of precipitation or dissolution of a given mineral and diel variations in the concentration of its constituents in Grape Creek.

Discussion

The mean concentrations of the major ions in Grape Creek and the trace elements aluminum, beryllium, boron, manganese, selenium, silica, sulfate, strontium, and zinc were within a factor of two of the mean concentrations of these constituents in samples from well MW3 (compare tables 4 and 7). None of these constituents exhibited diel variations. Water quality in well MW3 is assumed to be representative of groundwater influx to the creek along this reach. Because the creek was under base-flow conditions during the sampling period (essentially all of the water in the creek was derived from groundwater), the similarity in concentrations indicates that these constituents were derived primarily from groundwater efflux to the creek and that their concentrations were not substantially affected by chemical or biological reactions taking place in the creek or its underlying sediments. These data indicate that reactions involving aluminosilicate and sulfate minerals in the creek and sediments, although potentially occurring, are not substantial enough to affect the concentration of these constituents in the creek.

The mean concentrations of arsenic, barium, cobalt, iron, lead, nickel, vanadium, and probably nitrite in Grape Creek were at least a factor of two higher than the mean concentrations of these constituents in well MW3 (compare tables 4 and 7), indicating that these constituents were added to the creek partly by chemical and biological reactions taking place in the water column of the creek or its underlying sediments. The mean concentrations of cadmium, chromium, copper, and uranium in Grape Creek were at least a factor of two lower than the mean concentrations of these constituents in samples from well MW3, indicating that these constituents were removed from the creek by chemical and biological reactions taking place in the water column of the creek or its underlying sediments. Several of the constituents present at (mostly) higher or lower concentrations in Grape Creek exhibited diel variations, indicating that the processes that add these constituents to and remove them from the water column are of variable intensity during the course of a day.

Temperature, DO, pH, and specific conductance values all exhibited diel variations in Grape Creek during the sampling period, as did the concentrations of nitrite, barium, iron, lead, vanadium, and probably uranium. Concentrations of every constituent showed somewhat different timing of maximum and minimum values; however, two groups of constituents had generally similar trends. Temperature, specific conductance, DO (fig. 5*A*, 5*B*, 5*E*), nitrite (fig. 6), barium (fig. 8), lead (fig. 8), and uranium (fig. 9) tended to have maximum values during the afternoon and minimum values during the night. Iron (fig. 8), vanadium (fig. 8), and pH (fig. 5*C*) tended to have minimum values during the afternoon and maximum values during the night.

As expected, diel variations in the temperature of Grape Creek during the sampling period paralleled diel variations in air temperature (compare figs. 2 and 5*A*) and insolation, although air temperature was as much as 6.8 ^{o}C higher than creek temperature during most of the daylight hours and as much as 4.6 ^{o}C lower during most of the night. Water-temperature changes in the creek lagged behind air-temperature changes by 1–3 hours and insolation intensity by 2–4 hours. The temperature of the creek was about 4 to 10 ^{o}C higher than the temperature of groundwater measured at well MW3 (compare tables 4 and 7), and this may have affected precipitation and dissolution reactions where the two waters mix.

Diel variations in the specific conductance of Grape Creek during the sampling period indicate moderate diel variations in the total concentration of dissolved ionic constituents in the creek. Specific conductance had a generally inverse relation to pH (compare figs. 5*B* and 5*C*), indicating that lower pH enhances dissolution (or lessens precipitation) of minerals in the creek and increases the total concentration of dissolved ions. The mean specific conductance of groundwater at well MW3 was similar to the mean value for Grape Creek (compare tables 4 and 7), indicating that the groundwater flowing to the creek affects the chemistry of the creek. This interpretation is consistent with the similarity of concentrations of major ions in the creek and groundwater. However, specific conductance values in Grape Creek showed substantially more variation than they did in groundwater, indicating that water quality of the creek also is affected by diel processes occurring in the creek and, possibly, in the sediments beneath the creek.

DO is the most important dissolved gas in the surface-water environment because it is a product of photosynthesis, is essential to aerobic respiration, and many chemical and biological reactions are affected by the presence or absence of DO in water. The main factors affecting the concentration of DO in aquatic ecosystems are the exchange of DO between the water and the atmosphere, photosynthetic activity in the creek, which is related to insolation (fig. 2), and the breakdown of organic material by aquatic organisms (respiration) in the creek and underlying sediments (Radtke and others, 1998). DO patterns indicate that at daybreak (about 0600 hours), photosynthetic activity began producing DO in Grape Creek (fig. 5*E*) and concentrations of DO stopped decreasing. By about 1100 hours, photosynthetic DO production exceeded respiration, and the concentration of DO in the creek increased. By about 1615 hours, insolation and photosynthetic activity began to decrease (fig. 2), DO generation by photosynthesis began to be exceeded by DO consumption by respiration, and the concentration of DO decreased. Concentrations of DO continued to decrease through the evening and early morning as photosynthesis ceased and respiration continued. These patterns are typical of surface-water bodies in Illinois (Groschen and King, 2005).

One example of how DO can affect reactions involving other constituents is provided by the relation between DO and nitrite in Grape Creek (compare fig. 5*E* and fig. 6). The timing of the diel variation in concentration of nitrite was similar to that of DO, although trends in concentrations of nitrite appear to precede those of DO by 2 to 4 hours. This relation indicates that the nitrite is generated when concentrations of DO are high during the late morning and early evening, possibly resulting from the bacterially mediated oxidation of ammonium (given the pH of this water ammonium is likely to predominate over ammonia) described in equation 4. During the evening and night, anoxic respiration in the sediments and to some degree in the creek, likely produces the decrease in concentrations of DO observed in the creek. This period generally corresponds to the period when nitrite is removed from the water column, perhaps by the process of anaerobic ammonium oxidation (Schubert and others, 2006). The overall reaction for this process is represented by

$$NH_4^+ + NO_2^- \Leftrightarrow N_2 + H_2O. \qquad (8)$$

Additionally, the reduction of organic matter in sediments when DO is low (respiration) may result in the conversion of nitrite to ammonia according to

$$CH_2O + NO_2^- + 2H^+ \Leftrightarrow NH_4^+ + CO^2 \qquad (9)$$

Denitrification, the bacterially mediated conversion of nitrate to nitrogen gas through a series of intermediate compounds that include nitrite ($NO_3^- \rightarrow NO_2^- \rightarrow NO + N_2O \rightarrow N_{2\,(gas)}$), also may explain the absence of nitrite during low DO conditions. However, the absence of detectable concentrations of nitrate in the creek, although at a higher detection limit than for nitrite, does not clearly support this interpretation.

Nitrite was not reliably detected in groundwater at well MW3, indicating that the nitrite in the creek samples was not derived from recharging groundwater. In addition, no flow was observed in Grape Creek during the sampling period, indicating that nitrite in the creek samples was not derived from inflowing surface water. Therefore, nitrite was most likely added to, and removed from, the creek by chemical and biological processes occurring within the creek and the creek sediment. The 2 to 4 hour lag in the trends in concentrations of DO and nitrite indicates that at least some of the nitrite production and degradation is occurring in the creek sediments and that the timing is affected by the need to diffuse DO and nitrite into and out of the sediment into the water column.

The pH of groundwater at well MW3 (median 3.7) was somewhat higher than at Grape Creek (median of 3.3). However, the pH of most Midwestern streams typically is in the 6–8 range, and the low pH of Grape Creek at the site indicates that the creek pH is substantially affected by the pH of the influent groundwater. The diel variations in pH in the creek indicate that the pH of the creek also is affected by processes within the water column of the creek or the underlying sediments.

Trends in pH at Grape Creek during the sampling period (fig. 5*C*) are opposite the diel pH trends in most Midwestern streams, which have lowest pH in late morning and highest in late evening. This difference is due to the acidic nature of Grape Creek and the alkaline nature of most Midwestern streams and adjacent groundwater. Natural changes in pH in alkaline streams are affected primarily by variations in the intensity of photosynthesis and respiration. In most streams photosynthesis by aquatic organisms will cause pH to increase during the day, because photosynthesis consumes carbon dioxide, a weak (carbonic) acid in water, as described by equation 1. Respiration, whose effects are dominant at night, causes pH to decrease because this process generates carbon dioxide (equation 2). However, substantial concentrations of the mineral acid (H_2SO_4) derived from influent groundwater have resulted in a low pH for this creek, and it is likely that variations in the amount of carbonic acid generated in Grape Creek have little or no effect on pH. Alternate explanations of the diel variation in pH at Grape Creek during the sampling period are needed to explain the data.

The pH trends in Grape Creek may be the result of the photoreduction of Fe^{3+} to Fe^{2+}. During daylight hours in water with low pH and high concentrations of iron and sulfate, photoreduction of iron sulfate complexes generates hydrogen ions (equation 5) (Gammon and others, 2005a), which decreases pH. At night photoreduction ceases, reaction (5) reverses, and pH increases. Because all of the components of reaction (5) are in the aqueous phase, this reaction should have no direct effect on the total concentration of iron or sulfate in Grape Creek.

However, the generation of Fe^{2+} by photoreduction, as well as the presence of DO in the water column of Grape Creek, also may have promoted other reactions that would decrease pH and the concentration of iron, such as the formation of goethite described by equation 3. This interpretation is supported by the strong inverse correlation ($R^2 = -0.78$) between the concentrations of iron and the values for solar radiation. Concentrations of iron in the water column at acid mine drainage sites in the western U.S. exhibited low concentrations during the day and higher concentrations during the night (Gammons and others, 2005a). These diel trends have been attributed to the precipitation of hydrous ferric oxides, such as goethite (equation 3), during daylight hours when photoreduction is producing Fe^{2+} and photosynthesis is producing DO. Dissolution of other iron-containing minerals (such as $Fe(OH)_2$) and, possibly, less intense precipitation of iron oxides (such as hematite) and hydrous ferric oxides at night when there would be less DO and Fe^{2+} could result in increasing concentrations of these constituents in the water column (Gammons and others, 2005a and b; Jones and others, 2006). At pH values in Grape Creek during the sampling period (median 3.3), it is likely that schwertmannite also would precipitate (table 9; Bingham and others, 1996). The intensity of schwertmannite precipitation could potentially vary on a diel cycle. Schwertmannite then would transform to goethite, jarosite, or ferrihydrite over a period of months (Bingham and others, 1996; Acero and others, 2006). Such reactions appear to be a feasible explanation for the presence of goethite and jarosite in the sediments of Grape Creek (table 3) as well as the diel variations in concentration of iron observed during the sampling period. The strong correlation between the concentrations of iron and vanadium ($R^2 = 0.73$) indicates that vanadium is incorporated as a trace element into the goethite and other minerals that are affecting the diel variations in concentrations of iron (Peacock and Sherman, 2004).

The timing of the diel variations in the concentrations of barium (fig. 8), lead (fig. 8) and uranium (fig. 9) in Grape Creek were similar to each other as well as to the general timing of the diel variations in temperature (fig. 5*A*), specific conductance (fig. 5*B*), intensity of solar radiation (fig. 2), and concentration of DO (fig. 5*E*). Variations in the concentrations of lead, uranium, and other trace elements in surface water have been attributed to variations in their sorption onto and release from the mineral surfaces of hydrous iron oxides, such as goethite (McKnight and others, 1988; Francis and Dodge, 1990; Gammons and others, 2005b; Jang and others, 2008) and jarosite (Jones and others, 2006), or organic material (Schiller and others, 2006) under the influence of biologic activity, photoreduction, and variations in temperature, redox, and pH. The sorption of a cation (Pb^{2+}, for example) onto a sorption site (SOH) can be represented by

$$Pb^{2+} + SOH \Leftrightarrow SOPb^{+} + H^{+}. \qquad (10)$$

However, the concentrations of barium, lead, and uranium show a generally inverse relation with pH and concentrations of total iron (figs. 8 and 9). These trends indicate that the primary process that appears to be affecting pH and concentrations of iron in Grape Creek, the photoreduction-affected precipitation of hydrous ferric oxides and iron oxides, and perhaps dissolution of iron hydroxides and hydrous iron sulfates, was having the inverse effect on the concentrations of barium, lead, and uranium.

Concentrations of lead and uranium (but not barium) show a high to moderate degree of correlation with intensity of solar radiation ($R^2 = 0.70$ for lead, $R^2 = 0.59$ for uranium, $R^2 = 0.19$ for barium), indicating that diel variations in concentrations of lead and uranium in Grape Creek may be partly affected by their release to the water column as trace elements during competition with photoreduction-produced Fe^{2+} for cation exchange sites on goethite and other iron minerals. In addition, sorption of lead, uranium, and barium onto goethite and similar minerals decreases with decreasing pH (Dzombak and Morel, 1990; Cheng and others, 2004), as is indicated by equation 10. It is likely that diel variations in pH affected the amount of sorption and desorption of lead, uranium, and barium from goethite and similar minerals in Grape Creek and in the underlying sediment, which, in turn, likely affected their concentrations in the water column.

The data indicate that lead, uranium, and barium were removed from (or not incorporated into) cation exchange sites on goethite and, perhaps, other iron minerals during the day when Fe^{2+} likely was at higher concentrations in the creek water (and pH was lower), and were incorporated into the exchange sites during the evening and night when Fe^{2+} likely was at lower concentrations (and pH was higher). It is also possible that these constituents are incorporated as trace elements into minerals that could be preferentially precipitating at night (possibly schwertmannite) when Fe^{3+} may be more chemically active. The timing of the diel variations in concentrations of iron, barium, lead, and uranium in Grape Creek also show general agreement (or inverse agreement) with the timing of the diel variations in temperature, redox conditions (indicated by concentrations of DO), and biological activity (indicated by concentrations of DO and insolation values), indicating that these factors also affect constituent concentrations in Grape Creek.

Summary and Conclusions

To assess the potential for diel variations in concentrations of dissolved trace elements and other constituents in surface- and groundwater at Midwestern Superfund sites, the U.S. Geological Survey Illinois Water Science Center conducted an investigation, in cooperation with the U.S. Environmental Protection Agency, to identify and characterize diel variations in surface- and groundwater quality at the Hegeler Zinc Superfund site near Hegeler, Ill. The investigation was performed August 1–3, 2007.

Water-quality data of samples collected from well MW3 indicate stable, low pH, weakly oxidizing, geochemical conditions in the aquifer during the sampling period. With the exception of temperature and pH, no groundwater constituent exhibited diel variations in concentration. These data indicate that groundwater samples can be collected from this well at any time during the day without biasing the results.

Diel variations in water temperature in samples from well MW3 likely were caused by atmospheric temperature and solar warming of water in the above-ground sampling equipment and do not represent conditions in the aquifer. Diel variations in the pH measured at well MW3 likely reflect the effects of diel changes in atmospheric temperature and intensity of solar radiation on pH-altering reactions occurring in the flow-through cell where the measurements were taken and likely do not represent conditions in the aquifer. Water-quality data, mineral analysis, and geochemical modeling indicate that the low pH of water in samples from well MW3, as well as the high concentrations of iron and sulfate, likely are the result of the oxidation of sulfide minerals in the fill.

Acidic groundwater likely has enhanced the dissolution of numerous minerals in the aquifer and increased the solubility of the constituents released to the groundwater by that dissolution. These factors have contributed to the high concentrations of calcium, aluminum, beryllium, boron, cadmium, cobalt, lead, manganese, nickel, silica, strontium, vanadium, and zinc, and low concentrations of carbonate species in groundwater at the site relative to typical shallow groundwater in central Illinois.

Elevated concentrations of zinc in water from well MW3 may be derived from dissolution of sphalerite and gahnite. The elevated concentrations of calcium, magnesium, sodium, and silica may be derived partly from the dissolution of calcium, magnesium, and sodium from silicate minerals. The sources of the elevated concentrations of beryllium, boron, cadmium, cobalt, lead, manganese, nickel, strontium, and vanadium in groundwater from well MW3 may be from dissolution of minerals in which they are secondary or trace constituents.

Temperature, dissolved oxygen (DO), pH, and specific conductance values in Grape Creek all exhibited diel variations during the sampling period, as did the concentrations of nitrite, barium, iron, lead, vanadium, and, possibly, uranium. The processes responsible for these variations appear to occur in the water column of the creek or in the underlying sediments, rather than in recharging groundwater.

Concentrations in Grape Creek over the diel cycle varied by about an order of magnitude for nitrite and varied by about a factor of two for barium, iron, lead, vanadium, and uranium. Concentrations of every constituent showed different timing of maximum and minimum values, however, two groups of constituents had generally similar trends. Temperature, DO, specific conductance, nitrite, barium, lead, and uranium all tended to reach maximum values during the afternoon and minimum values during the night. Iron, vanadium, and pH all tended to reach minimum values during the afternoon and maximum values during the night. These factors should be taken into account when obtaining samples for the analysis of surface-water quality.

The diel variations in the temperature and the concentration of DO in Grape Creek are typical of Illinois surface water. Temperature variations were affected by variations in air temperature and insolation. Variations in concentrations of DO reflect the relative intensity of photosynthetic activity and respiration in the creek.

Diel variations in concentrations of nitrite and their relation to DO in Grape Creek indicate that the nitrite typically is generated by the oxidation of ammonium. The process(es) responsible for the removal of nitrite could not be conclusively determined from the data collected for this investigation, but anaerobic ammonium oxidation or reduction to ammonium as part of the respiration process is consistent with the available data.

The timing of the trends in the pH of Grape Creek is opposite the diel pH trends in most Midwestern streams. pH trends in Grape Creek appear to be the result of the photoreduction of Fe^{3+} to Fe^{2+}.

Variations in the amount of precipitation and dissolution of iron-bearing minerals such as goethite, and, perhaps, schwertmannite and jarosite, in the creek sediments appear to affect the diel variations in the concentrations of iron and vanadium observed during the sampling period. The intensity of these processes appears to be affected by the intensity of insolation and the presence of DO as well as pH, temperature, and, perhaps, biological activity. The concentrations of lead, uranium, and barium in Grape Creek may be affected by competition with Fe^{2+} for sorption or cation exchange sites on goethite and other iron minerals as well as the effects of changes in pH on their capacity for sorption. Concentrations of lead, uranium, and barium also may be affected by the dissolution and precipitation of nonferric minerals that are sensitive to pH, temperature, oxidation-reduction potential, and biological activity.

The results of this investigation indicate that sampling strategies for nutrients, metals, and other constituents in surface water at Superfund sites (and other areas of investigation) affected by acid drainage, as well as at areas that are not so affected, should consider the effects of diel variations on water quality. Depending on the goals of the investigation, sampling strategies should include collection of grab samples on a diel basis, collection of grab samples at consistent times during the day (or night) depending on the constituents of concern, or collection of composite samples over the course of a day. The results also indicate that identification of diel trends would be facilitated by minimizing sources of data variability in the lab, such as the amount of sample dilution.

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Table 2. Bulk chemistry of samples from the slag pile and stream sediment, Hegeler Zinc Superfund site, near Hegeler, Illinois (data from Nadine Piatak, U.S. Geological Survey, written commun., 2007, 2008).

[SS in sample number denotes sediment sample, see also table 1, other samples are of slag; mg/kg, milligrams per kilogram; <, less than; -, not analyzed]

Sample number	Aluminum	Calcium	Iron	Potassium	Magnesium	Sodium	Sulfur	Titanium	Silver	Arsenic	Barium	Beryllium	Bismuth
	(weight percent)	(weight percent)	(weight percent)	(weight percent)	(weight percent)	(weight percent)	(weight percent)	(weight percent)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
IL-HG-1	8.92	5.64	13.20	1.24	0.36	0.85	2.68	0.53	2	32	611	11.3	0.12
IL-HG-2	.20	.17	.76	.05	.04	.05	1.91	.04	1	45	76	.4	<.04
IL-HG-3	8.66	2.38	13.30	1.16	.73	1.02	.45	.68	10	7	866	6.9	.07
IL-HG-3 duplicate	9.15	2.43	13.40	1.16	.77	1.06	.47	.69	9	4	851	8.8	.06
IL-HG-5	6.45	2.05	13.20	1.00	.36	.55	.54	.35	4	31	471	9	.36
IL-HG-9a	11.40	8.61	14.40	1.39	.72	.79	.47	.62	<1	5	1,040	18	<.04
IL-HG-9b	14.10	1.20	5.25	3.34	.50	2.42	.12	.68	<1	6	215	5.8	<.04
IL-HG-9c	10.60	9.92	10.50	1.38	.66	.70	.21	.56	<1	1	835	17	<.04
IL-HG-9d	11.00	8.63	10.30	1.42	.65	.64	.69	.57	<1	5	1,170	16.3	<.04
IL-HG-10	9.71	6.25	16.50	1.45	.54	.81	.82	.55	<1	3	788	19	<.04
IL-HG-11	11.00	7.89	16.20	1.33	.59	.70	.57	.60	<1	5	987	17	<.04
IL-HG-1-SS-10m	3.63	.28	19.50	1.06	.23	.36	1.84	.10	<1	85	262	2.5	.16
IL-HG-1-SS-80m	4.11	.34	16.50	1.26	.26	.47	1.46	.12	<1	66	313	2.3	.17
IL-HG-1-SS-hp	1.86	.11	37.00	.56	.08	.15	2.33	.04	<1	72	102	2.3	.07
IL-HG-2-SS-10m	5.81	.65	2.78	1.45	.43	.58	.36	.17	<1	14	427	4.1	.23
IL-HG-2-SS-80m	5.92	.69	2.72	1.57	.43	.65	.36	.18	<1	14	446	3.9	.23

Table 2. Bulk chemistry of samples from the slag pile and stream sediment, Hegeler Zinc Superfund site, near Hegeler, Illinois (data from Nadine Piatak, U.S. Geological Survey, written commun., 2007, 2008). —Continued

[SS in sample number denotes sediment sample, see also table 1, other samples are of slag; mg/kg, milligrams per kilogram; <, less than; -, not analyzed]

Sample number	Cadmium	Cerium	Cobalt	Chromium	Cesium	Copper	Gallium	Indium	Lanthanum	Lithium	Manganese	Molybdenum	Niobium
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
IL-HG-1	1.5	90.2	20	96	7	109	14.2	0.04	42.7	101	553	21.2	19.3
IL-HG-2	191	9.51	8.5	4	<5	291	39.3	.17	4.9	5	77	1.9	1.8
IL-HG-3	.8	141	242	71	6	6,360	338	.37	75.1	138	2,580	37.3	24.4
IL-HG-3 duplicate	.3	120	231	109	6	6,270	348	.39	62.5	119	2,550	36.3	22.7
IL-HG-5	18.9	59.5	23.8	84	5	274	38	.13	28.8	87	702	17	13.4
IL-HG-9a	48.1	116	17.7	77	<5	47.6	2.72	<.02	49.3	127	1,040	18.8	25
IL-HG-9b	2.9	97.7	13.3	103	12	66.4	49.7	<.02	48.5	234	296	2.4	26.2
IL-HG-9c	16.4	112	14.1	79	<5	16	2.89	<.02	47.7	140	1,110	9.97	22.9
IL-HG-9d	18.9	126	18.5	73	<5	29.2	2.98	<.02	52.6	124	867	12.9	23.3
IL-HG-10	3	96.4	17.5	97	6	33.6	3.25	<.02	40.4	127	684	13.4	22.5
IL-HG-11	2.8	125	26.9	100	<5	40.8	2.51	<.02	53.1	133	851	18.7	24.2
IL-HG-1-SS-10m	10.3	34.4	2.9	26	<5	10.6	6.44	.02	15.3	23	76	.93	3.9
IL-HG-1-SS-80m	9.7	38.5	3.3	29	<5	11.2	7.21	.03	19.1	24	87	.96	4.6
IL-HG-1-SS-hp	1.1	16.2	1.2	13	<5	.5	2.98	<.02	7.3	8	31	.54	1.8
IL-HG-2-SS-10m	28.6	83.8	8	37	<5	40	10.2	.04	32.8	58	175	1.27	6.4
IL-HG-2-SS-80m	24.8	86.9	7.7	38	<5	38.9	10.3	.04	34.5	60	172	1.16	7

Table 2. Bulk chemistry of samples from the slag pile and stream sediment, Hegeler Zinc Superfund site, near Hegeler, Illinois (data from Nadine Piatak, U.S. Geological Survey, written commun., 2007, 2008). —Continued

[SS in sample number denotes sediment sample, see also table 1, other samples are of slag; mg/kg, milligrams per kilogram; <, less than; -, not analyzed]

Sample number	Nickel (mg/kg)	Phosphorous (mg/kg)	Lead (mg/kg)	Rubidium (mg/kg)	Antimony (mg/kg)	Scandium (mg/kg)	Tin (mg/kg)	Strontium (mg/kg)	Tellurium (mg/kg)	Thorium (mg/kg)	Thallium (mg/kg)	Uranium (mg/kg)
IL-HG-1	68.2	610	325	89.6	12.8	18.7	3.2	248	<0.1	15.8	0.5	6.7
IL-HG-2	25.2	100	45.4	3.5	4.76	1.8	1.4	19.4	<.1	1.7	<.1	.6
IL-HG-3	107	1,130	255	72.3	2.26	25.9	1	296	<.1	23.6	<.1	10
IL-HG-3 duplicate	99.2	1,090	228	71	2.53	27.3	.6	298	<.1	22.6	<.1	10.7
IL-HG-5	59.3	690	711	73.2	9.01	16.4	3.8	170	<.1	11.1	1	7.4
IL-HG-9a	34.2	550	19.6	83.2	.27	33	.2	456	<.1	18.6	.1	15.9
IL-HG-9b	24.3	2,130	45.6	248	.5	22.4	.4	273	<.1	18.5	.2	10.7
IL-HG-9c	25.5	550	1.9	85.2	<.05	32.4	<.1	454	<.1	18.1	<.1	14.6
IL-HG-9d	35.8	730	6.6	89.3	.16	31.9	.1	583	<.1	18.4	<.1	16.4
IL-HG-10	31.3	450	7.6	107	.21	27.9	1.4	294	<.1	16.9	<.1	10.2
IL-HG-11	57.6	630	48.7	88.7	.18	31	.2	443	<.1	19.1	<.1	10.6
IL-HG-1-SS-10m	9	1,660	43.3	48.8	1.07	4.5	1	57.3	<.1	4.4	.4	1.1
IL-HG-1-SS-80m	11.5	1,470	42.4	57.2	.99	5.2	2.2	70.6	<.1	5.3	.5	1.3
IL-HG-1-SS-hp	<.5	960	25.9	21.6	.5	1.9	.4	24.1	<.1	1.9	.2	.5
IL-HG-2-SS-10m	30.8	930	40.8	76.6	1.49	7.6	1.5	94.5	<.1	7.5	.7	2.5
IL-HG-2-SS-80m	30.5	910	39.3	80.4	1.39	7.9	2.2	103	<.1	8.4	.8	2.5

Table 2. Bulk chemistry of samples from the slag pile and stream sediment, Hegeler Zinc Superfund site, near Hegeler, Illinois (data from Nadine Piatak, U.S. Geological Survey, written commun., 2007, 2008). —Continued

[SS in sample number denotes sediment sample, see also table 1, other samples are of slag; mg/kg, milligrams per kilogram; <, less than; -, not analyzed]

Sample number	Vanadium	Tungsten	Yttrium	Zinc	Carbonate carbon	Organic carbon
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(weight percent)	(weight percent)
IL-HG-1	156	2.7	31.1	2,000	-	-
IL-HG-2	6	.4	4.5	284,400	-	-
IL-HG-3	125	4.3	54.3	14,900	-	-
IL-HG-3 duplicate	148	4.0	57.5	15,400	0.01	4.33
IL-HG-5	120	2.3	34	8,960	-	-
IL-HG-9a	190	1.9	68	2,370	-	-
IL-HG-9b	120	2.0	36.4	11,400	-	-
IL-HG-9c	170	1.4	67.4	1,690	-	-
IL-HG-9d	148	1.4	69.9	1,220	-	-
IL-HG-10	166	1.9	55.5	212	-	-
IL-HG-11	178	1.7	61.4	1,020	-	-
IL-HG-1-SS-10m	110	.4	15.4	2,150	.01	2.52
IL-HG-1-SS-80m	99	.5	16.8	1,410	.02	2.1
IL-HG-1-SS-hp	91	.2	7.3	1,060	.01	1.23
IL-HG-2-SS-10m	60	.6	34.4	3,610	.05	3.09
IL-HG-2-SS-80m	60	.8	34.8	3,460	.04	2.4

Table 5. Pearson product-moment correlation coefficients for selected constituents in water samples from well MW3, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007.

[Positive correlations greater than 0.70 in gray and boldface; -, indicates redundant cell]

	Magnesium	Potassium	Sodium	Sulfate	Chloride	Silica	Aluminum	Arsenic	Barium	Beryllium	Boron	Cadmium	Chromium	Cobalt
Calcium	**0.92**	0.49	**0.74**	0.05	0.04	**0.72**	0.02	0.00	-0.08	0.08	0.01	0.00	0.01	0.08
Magnesium	-	.42	**.80**	.02	.04	.63	.01	.00	-.07	.09	.01	.00	.01	.08
Potassium	-	-	.46	.01	.03	.36	.00	-.05	-.09	.12	-.02	.17	-.02	.04
Sodium	-	-	-	.01	.03	.57	.00	.00	-.06	.07	.00	.01	.00	.04
Sulfate	-	-	-	-	.33	-.06	-.01	-.06	.00	.00	.00	.10	-.08	.00
Chloride	-	-	-	-	-	.02	.00	.03	-.09	.15	.00	.01	.00	.07
Silica	-	-	-	-	-	-	.00	.00	-.02	.01	.00	.00	.00	.00
Aluminum	-	-	-	-	-	-	-	-.01	.04	-.03	**.75**	.00	.00	-.04
Arsenic	-	-	-	-	-	-	-	-	-.06	.22	-.01	.04	.14	.38
Barium	-	-	-	-	-	-	-	-	-	-.64	.01	.00	.00	-.40
Beryllium	-	-	-	-	-	-	-	-	-	-	-.02	.01	.01	.68
Boron	-	-	-	-	-	-	-	-	-	-	-	-.03	.00	.02
Cadmium	-	-	-	-	-	-	-	-	-	-	-	-	-.19	.03
Chromium	-	-	-	-	-	-	-	-	-	-	-	-	-	.09
Cobalt	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Copper	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Iron	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Lead	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Manganese	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Nickel	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Selenium	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Strontium	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Vanadium	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Zinc	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Uranium	-	-	-	-	-	-	-	-	-	-	-	-	-	-
pH	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temperature	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Specific conductance	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Dissolved oxygen	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Copper	Iron	Lead	Manganese	Nickel	Selenium	Strontium	Vanadium	Zinc	Uranium	pH	Temperature	Specific conductance	Dissolved oxygen	Oxidation-reduction potential
0.00	0.07	-0.04	0.09	0.06	0.00	0.00	0.00	0.07	0.01	0.00	0.00	0.00	0.00	0.00
.01	.08	-.04	.08	.07	.00	.00	-.01	.07	-.01	.00	.00	.00	-.04	.02
.20	-.01	.00	.03	.01	-.05	.09	-.21	.00	.04	-.03	-.02	.00	.00	.32
.05	.01	-.03	.03	.03	-.04	.04	-.07	.03	.00	-.05	-.01	.00	-.11	.16
.12	-.18	.01	-.02	-.02	-.08	.08	-.24	-.01	.06	-.03	-.01	.04	-.02	.24
.03	.00	.06	.08	.06	.01	.07	.00	.00	.01	-.07	.01	-.09	-.04	.00
-.04	.12	.00	.01	.00	.00	.00	.01	.02	.00	.00	.00	-.03	.00	-.02
-.06	.04	.00	-.04	-.03	.01	-.02	.02	.60	.01	.00	-.02	.01	.02	-.03
.00	.19	.01	.51	.45	.50	.07	.09	-.09	-.06	.04	.14	-.02	-.01	-.25
-.21	.02	.01	-.44	-.31	-.04	-.16	.24	.00	.02	.16	.07	.13	.00	-.10
.37	.00	.00	**.73**	.60	.15	.30	-.23	.00	.04	-.06	.00	-.02	-.01	.05
-.06	.01	-.02	-.02	.00	.00	-.04	.02	**.73**	.01	.00	.03	.00	.00	-.02
.26	-.18	.08	.00	.00	-.15	.49	-.22	.00	**.75**	-.02	.00	.00	-.02	.31
.00	.10	-.03	.13	.17	.11	-.13	.07	-.03	.28	.02	.04	.11	.00	-.14
.30	.00	-.04	**.93**	**.94**	.27	.29	-.06	.00	.00	.00	.06	.00	-.07	.00
-	-.28	.01	.16	.20	.01	.28	-.52	-.05	.03	-.15	-.02	.00	-.03	.52
-	-	-.03	.05	.03	.25	-.03	.27	.03	-.09	.03	.00	.04	.01	-.19
-	-	-	-.03	-.08	.00	.01	-.03	-.05	.09	-.04	-.09	-.02	.04	.04
-	-	-	-	**.90**	.37	.20	-.03	.00	.05	.00	.04	.00	-.02	-.02
-	-	-	-	-	.36	.18	-.01	.00	-.05	.01	.08	.00	-.06	.02
-	-	-	-	-	-	.00	.13	-.01	-.12	.12	.15	.00	.01	-.32
-	-	-	-	-	-	-	-.13	.00	.37	-.01	.00	-.08	-.16	.10
-	-	-	-	-	-	-	-	.01	-.02	.26	.08	-.01	.00	-.65
-	-	-	-	-	-	-	-	-	.00	-.01	-.06	.00	.00	.01
-	-	-	-	-	-	-	-	-	-	.00	.00	-.05	-.04	.08
-	-	-	-	-	-	-	-	-	-	-	.40	.01	.00	-.44
-	-	-	-	-	-	-	-	-	-	-	-	.00	-.07	-.22
-	-	-	-	-	-	-	-	-	-	-	-	-	.01	.00
-	-	-	-	-	-	-	-	-	-	-	-	-	-	.00

Table 6. Summary of pH, temperature, and saturation indexes for selected minerals computed for samples from well MW3, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007.

[PHREEQC, pH–redox–equilibrium-equations in C code; CDT, Central Daylight Time; na, not applicable; Al, aluminum; Ca, calcium; O, oxygen; H, hydrogen; all PHREEQC modeling of groundwater samples was done with temperature at 15.5 degrees Celsius and a pH of 3.68; see appendix 4 for mineral formulas]

Date (month/day/year)	CDT (hour:minute)	pH standard units)	Water temperature (degrees Celsius)	Saturation indexes calculated by PHREEQC[a]								
				Minerals in the Lawrence Livermore National Laboratory database[b]								Schwertmannite[c]
				Clinochlor-14A	Clinochlor-7A	Fayalite	$Fe(OH)_2$	Hercynite	Jadeite	Ca-Al pyroxene	Spinel	
8/1/2007	12:45	3.85	16.0	-44.2	-47.7	-27.9	-17.1	-18.7	-6.06	-20.9	-21.2	7.4
8/1/2007	14:15	4.22	16.3	-44.3	-47.7	-28.0	-17.1	-18.7	-6.07	-21.0	-21.2	7.1
8/1/2007	15:45	4.06	16.3	-44.3	-47.7	-28.0	-17.1	-18.7	-6.07	-20.9	-21.2	7.5
8/1/2007	17:15	3.95	16.0	-44.4	-47.8	-28.0	-17.1	-18.7	-6.11	-20.9	-21.2	7.2
8/1/2007	18:45	3.77	16.0	-44.3	-47.7	-28.0	-17.1	-18.7	-6.07	-20.9	-21.2	7.1
8/1/2007	20:15	3.74	15.7	-44.5	-47.9	-28.1	-17.2	-18.8	-6.16	-21.0	-21.2	6.7
8/1/2007	21:45	3.71	15.6	-44.3	-47.7	-28.1	-17.2	-18.7	-6.07	-20.9	-21.1	6.8
8/1/2007	23:15	3.72	15.5	-44.3	-47.8	-28.3	-17.3	-18.8	-6.09	-20.9	-21.2	7.1
8/2/2007	0:45	3.7	15.6	-44.3	-47.7	-28.1	-17.1	-18.7	-6.08	-20.9	-21.2	6.7
8/2/2007	2:15	3.7	15.5	-44.2	-47.6	-28.1	-17.2	-12.8	-6.03	-20.9	-21.2	7.0
8/2/2007	3:45	3.68	15.5	-44.1	-47.6	-28.0	-17.1	-12.9	-5.99	-20.9	-21.2	7.1
8/2/2007	5:15	3.68	15.5	-44.4	-47.8	-28.2	-17.2	-12.8	-6.12	-21.0	-21.2	6.7
8/2/2007	6:45	3.67	15.6	-44.3	-47.8	-28.0	-17.1	-18.7	-6.10	-20.9	-21.2	7.3
8/2/2007	8:15	3.81	15.9	-44.3	-47.8	-28.1	-17.2	-18.7	-6.10	-20.9	-21.2	6.9
8/2/2007	9:45	3.88	16.0	-44.3	-47.7	-28.1	-17.2	-18.7	-6.07	-20.9	-21.2	6.8
8/2/2007	11:15	4.04	16.0	-44.4	-47.8	-28.1	-17.1	-18.8	-6.12	-21.0	-21.2	6.9
8/2/2007	12:45	3.81	16.0	-44.4	-47.8	-28.1	-17.1	-18.7	-6.12	-21.0	-21.2	7.0
8/2/2007	14:15	3.78	16.7	-44.3	-47.7	-28.1	-17.1	-18.8	-6.10	-21.0	-21.2	6.9
8/2/2007	15:45	3.96	16.2	-44.2	-47.7	-28.0	-17.1	-18.8	-6.08	-21.0	-21.2	7.0
8/2/2007	17:15	3.72	16.2	-44.3	-47.8	-28.1	-17.2	-18.7	-6.08	-20.9	-21.2	6.7

Table 6. Summary of pH, temperature, and saturation indexes for selected minerals computed for samples from well MW3, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. —Continued

[PHREEQC, pH–redox–equilibrium-equations in C code; CDT, Central Daylight Time; na, not applicable; Al, aluminum; Ca, calcium; O, oxygen; H, hydrogen; all PHREEQC modeling of groundwater samples was done with temperature at 15.5 degrees Celsius and a pH of 3.68; see appendix 4 for mineral formulas]

Date (month/day/ year)	CDT (hour: minute)	pH standard units)	Water temperature (degrees Celsius)	Saturation indexes calculated by PHREEQC[a]								
				Minerals in the Lawrence Livermore National Laboratory database[b]								Schwertmannite[c]
				Clinochlor-14A	Clinochlor-7A	Fayalite	$Fe(OH)_2$	Hercynite	Jadeite	Ca-Al pyroxene	Spinel	
8/2/2007	18:45	3.74	15.9	-44.3	-47.7	-30.1	-18.1	-19.7	-6.09	-21.0	-21.2	na
8/2/2007	20:15	3.71	15.7	-44.2	-47.7	-28.0	-17.1	-12.8	-6.05	-20.9	-21.2	7.1
8/2/2007	21:45	3.68	15.7	-44.3	-47.8	-28.1	-17.1	-18.8	-6.10	-21.0	-21.2	6.9
8/2/2007	23:15	3.61	15.6	-44.3	-47.7	-28.1	-17.2	-18.7	-6.08	-20.9	-21.2	6.8
8/3/2007	0:45	3.68	15.6	-44.3	-47.8	-28.2	-17.2	-18.8	-6.11	-21.0	-21.2	6.8
8/3/2007	2:15	3.61	15.6	-44.2	-47.7	-28.1	-17.2	-18.7	-6.06	-20.9	-21.2	6.6
8/3/2007	3:45	3.66	15.5	-44.3	-47.8	-28.1	-17.1	-18.7	-6.08	-21.0	-21.2	6.8
8/3/2007	5:15	3.64	15.6	-44.3	-47.8	-28.1	-17.2	-18.8	-6.10	-21.0	-21.3	6.9
8/3/2007	6:45	3.69	15.7	-44.3	-47.7	-28.1	-17.1	-18.7	-6.08	-21.0	-21.2	6.9
8/3/2007	8:15	3.77	15.8	-44.4	-47.8	-28.1	-17.1	-18.7	-6.11	-21.0	-21.2	6.9
8/3/2007	9:45	3.91	15.9	-44.3	-47.7	-28.1	-17.2	-18.8	-6.07	-20.9	-21.2	6.8
8/3/2007	11:15	3.88	16.0	-44.3	-47.7	-28.1	-17.2	-18.7	-6.06	-20.9	-21.2	6.8

Table 6. Summary of pH, temperature, and saturation indexes for selected minerals computed for samples from well MW3, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. —Continued

[PHREEQC, pH–redox–equilibrium-equations in C code; CDT, Central Daylight Time; na, not applicable; Al, aluminum; Ca, calcium; O, oxygen; H, hydrogen; all PHREEQC modeling of groundwater samples was done with temperature at 15.5 degrees Celsius and a pH of 3.68; see appendix 4 for mineral formulas]

Date (month/day/year)	CDT (hour:minute)	pH standard units)	Water temperature (degrees Celsius)	Saturation indexes calculated by PHREEQC[a]									
				Minerals in the Lawrence Livermore National Laboratory database[b]									
				Albite	Alunite	Anorthite	Barite	Chalcedony	Cuprous Ferrite	$Fe(OH)_3(a)$	Forsterite	Goethite	Gypsum
8/1/2007	12:45	3.85	16.0	-5.3	1.9	-13.7	-0.24	0.94	-4.3	0.38	-24.3	5.9	-0.023
8/1/2007	14:15	4.22	16.3	-5.3	1.9	-13.7	-.23	.95	-4.3	.34	-24.3	5.9	-.031
8/1/2007	15:45	4.06	16.3	-5.4	2.0	-13.7	-.16	.94	-4.4	.39	-24.3	5.9	-.026
8/1/2007	17:15	3.95	16.0	-5.4	2.0	-13.7	-.16	.91	-4.4	.36	-24.3	5.9	-.056
8/1/2007	18:45	3.77	16.0	-5.4	2.0	-13.7	-.16	.93	-4.4	.34	-24.3	5.9	-.036
8/1/2007	20:15	3.74	15.7	-5.5	1.8	-13.8	-.24	.91	-4.3	.30	-24.3	5.8	-.067
8/1/2007	21:45	3.71	15.6	-5.4	2.0	-13.6	-.24	.93	-4.4	.31	-24.3	5.9	-.038
8/1/2007	23:15	3.72	15.5	-5.4	2.0	-13.7	-.24	.93	-4.5	.35	-24.3	5.9	-.033
8/2/2007	0:45	3.7	15.6	-5.4	2.0	-13.7	-.24	.93	-4.3	.30	-24.3	5.8	-.027
8/2/2007	2:15	3.7	15.5	-5.3	2.0	-13.7	-.16	.95	-4.3	.33	-24.3	5.9	-.013
8/2/2007	3:45	3.68	15.5	-5.2	1.9	-13.6	-.23	.97	-4.4	.34	-24.2	5.9	.008
8/2/2007	5:15	3.68	15.5	-5.4	1.9	-13.7	-.16	.91	-4.4	.30	-24.3	5.8	-.058
8/2/2007	6:45	3.67	15.6	-5.4	1.9	-13.7	-.16	.92	-4.3	.37	-24.3	5.9	-.047
8/2/2007	8:15	3.81	15.9	-5.4	2.0	-13.7	-.16	.92	-4.3	.32	-24.3	5.9	-.046
8/2/2007	9:45	3.88	16.0	-5.4	2.0	-13.7	-.16	.93	-4.3	.31	-24.3	5.9	-.033
8/2/2007	11:15	4.04	16.0	-5.4	1.8	-13.8	-.16	.93	-4.3	.32	-24.3	5.9	-.039
8/2/2007	12:45	3.81	16.0	-5.4	1.9	-13.7	-.16	.91	-4.3	.33	-24.3	5.9	-.054
8/2/2007	14:15	3.78	16.7	-5.4	1.9	-13.7	-.16	.93	-4.3	.32	-24.3	5.9	-.030
8/2/2007	15:45	3.96	16.2	-5.4	1.9	-13.7	-.16	.94	-4.3	.33	-24.3	5.9	-.005
8/2/2007	17:15	3.72	16.2	-5.4	1.9	-13.7	-.34	.93	-4.2	.30	-24.3	5.8	-.026
8/2/2007	18:45	3.74	15.9	-5.4	1.9	-13.7	-.34	.93	na	na	-24.3	4.9	-.037

Table 6. Summary of pH, temperature, and saturation indexes for selected minerals computed for samples from well MW3, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. —Continued

[PHREEQC, pH–redox–equilibrium-equations in C code; CDT, Central Daylight Time; na, not applicable; Al, aluminum; Ca, calcium; O, oxygen; H, hydrogen; all PHREEQC modeling of groundwater samples was done with temperature at 15.5 degrees Celsius and a pH of 3.68; see appendix 4 for mineral formulas]

Date (month/day/ year)	CDT (hour: minute)	pH standard units)	Water temperature (degrees Celsius)	Saturation indexes calculated by PHREEQC[a]									
				Minerals in the Lawrence Livermore National Laboratory database[b]									
				Albite	Alunite	Anorthite	Barite	Chalcedony	Cuprous Ferrite	$Fe(OH)_3$(a)	Forsterite	Goethite	Gypsum
8/2/2007	20:15	3.71	15.7	-5.3	2.0	-13.7	-0.24	0.94	-4.2	0.34	-24.3	5.9	-0.008
8/2/2007	21:45	3.68	15.7	-5.4	1.9	-13.7	-.34	.93	-4.3	.32	-24.3	5.9	-.024
8/2/2007	23:15	3.61	15.6	-5.4	1.9	-13.7	-.24	.93	-4.3	.30	-24.3	5.8	-.025
8/3/2007	0:45	3.68	15.6	-5.4	1.9	-13.7	-.24	.92	-4.3	.31	-24.3	5.9	-.045
8/3/2007	2:15	3.61	15.6	-5.3	2.0	-13.7	-.24	.94	-4.4	.28	-24.3	5.8	-.019
8/3/2007	3:45	3.66	15.5	-5.4	1.9	-13.7	-.16	.93	-4.3	.31	-24.3	5.8	-.038
8/3/2007	5:15	3.64	15.6	-5.4	1.8	-13.7	-.34	.94	-4.3	.31	-24.3	5.9	-.025
8/3/2007	6:45	3.69	15.7	-5.4	1.9	-13.7	-.34	.93	-4.3	.32	-24.3	5.9	-.026
8/3/2007	8:15	3.77	15.8	-5.4	1.9	-13.7	-.16	.92	-4.2	.32	-24.3	5.9	-.047
8/3/2007	9:45	3.91	15.9	-5.3	1.9	-13.7	-.16	.94	-4.4	.30	-24.3	5.8	-.032
8/3/2007	11:15	3.88	16.0	-5.3	2.0	-13.7	-.16	.93	-4.4	.30	-24.3	5.8	-.039

Table 6. Summary of pH, temperature, and saturation indexes for selected minerals computed for samples from well MW3, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. —Continued

[PHREEQC, pH–redox–equilibrium-equations in C code; CDT, Central Daylight Time; na, not applicable; Al, aluminum; Ca, calcium; O, oxygen; H, hydrogen; all PHREEQC modeling of groundwater samples was done with temperature at 15.5 degrees Celsius and a pH of 3.68; see appendix 4 for mineral formulas]

Date (month/day/year)	CDT (hour:minute)	pH standard units)	Water temperature (degrees Celsius)	Saturation indexes calculated by PHREEQC[a]									
				Minerals in the Lawrence Livermore National Laboratory database[b]									
				Hematite	Jarosite (ss)	Jurbanite	Magnetite	Potassium (mica)	Potassium (feldpsar)	SiO$_2$(a)	Sphalerite	ZnS(a)	Diopside
8/1/2007	12:45	3.85	16.0	13.8	6.2	0.74	2.9	-1.4	-3.8	0.07	-129	-131	-17.2
8/1/2007	14:15	4.22	16.3	13.7	6.1	.72	2.8	-1.4	-3.8	.07	-129	-131	-17.2
8/1/2007	15:45	4.06	16.3	13.8	6.3	.74	2.9	-1.4	-3.8	.06	-129	-132	-17.2
8/1/2007	17:15	3.95	16.0	13.8	6.1	.75	2.8	-1.4	-3.9	.04	-129	-131	-17.3
8/1/2007	18:45	3.77	16.0	13.7	6.1	.75	2.8	-1.4	-3.8	.06	-129	-131	-17.2
8/1/2007	20:15	3.74	15.7	13.7	5.9	.70	2.7	-1.5	-3.9	.04	-129	-131	-17.3
8/1/2007	21:45	3.71	15.6	13.7	6.0	.77	2.7	-1.4	-3.8	.05	-129	-131	-17.2
8/1/2007	23:15	3.72	15.5	13.7	6.1	.75	2.7	-1.4	-3.8	.06	-130	-132	-17.2
8/2/2007	0:45	3.7	15.6	13.6	6.0	.74	2.7	-1.4	-3.8	.05	-128	-131	-17.2
8/2/2007	2:15	3.7	15.5	13.7	6.1	.75	2.7	-1.3	-3.8	.07	-129	-132	-17.2
8/2/2007	3:45	3.68	15.5	13.7	6.2	.73	2.8	-1.3	-3.7	.10	-129	-132	-17.1
8/2/2007	5:15	3.68	15.5	13.7	5.9	.73	2.6	-1.5	-3.9	.04	-129	-132	-17.3
8/2/2007	6:45	3.67	15.6	13.8	6.2	.74	2.8	-1.4	-3.9	.05	-129	-132	-17.2
8/2/2007	8:15	3.81	15.9	13.7	6.0	.75	2.7	-1.4	-3.9	.05	-129	-131	-17.3
8/2/2007	9:45	3.88	16.0	13.7	6.0	.75	2.7	-1.4	-3.8	.05	-129	-131	-17.2
8/2/2007	11:15	4.04	16.0	13.7	6.0	.70	2.7	-1.5	-3.9	.05	-129	-131	-17.2
8/2/2007	12:45	3.81	16.0	13.7	6.1	.73	2.8	-1.4	-3.9	.04	-129	-131	-17.3
8/2/2007	14:15	3.78	16.7	13.7	6.0	.71	2.7	-1.5	-3.9	.06	-129	-131	-17.2
8/2/2007	15:45	3.96	16.2	13.7	6.1	.73	2.7	-1.4	-3.8	.07	-129	-131	-17.2
8/2/2007	17:15	3.72	16.2	13.6	6.0	.74	2.7	-1.4	-3.8	.05	-129	-131	-17.2
8/2/2007	18:45	3.74	15.9	11.7	3.1	.73	na	-1.4	-3.9	.05	-129	-131	-17.2

Table 6. Summary of pH, temperature, and saturation indexes for selected minerals computed for samples from well MW3, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. —Continued

[PHREEQC, pH–redox–equilibrium-equations in C code; CDT, Central Daylight Time; na, not applicable; Al, aluminum; Ca, calcium; O, oxygen; H, hydrogen; all PHREEQC modeling of groundwater samples was done with temperature at 15.5 degrees Celsius and a pH of 3.68; see appendix 4 for mineral formulas]

Date (month/day/ year)	CDT (hour: minute)	pH standard units)	Water temperature (degrees Celsius)	Saturation indexes calculated by PHREEQC[a]									
				Minerals in the Lawrence Livermore National Laboratory database[b]									
				Hematite	Jarosite (ss)	Jurbanite	Magnetite	Potassium (mica)	Potassium (feldpsar)	SiO_2(a)	Sphalerite	ZnS(a)	Diopside
8/2/2007	20:15	3.71	15.7	13.7	6.1	0.76	2.8	-1.4	-3.8	0.06	-128	-131	-17.2
8/2/2007	21:45	3.68	15.7	13.7	6.1	.71	2.7	-1.5	-3.8	.06	-129	-131	-17.2
8/2/2007	23:15	3.61	15.6	13.7	6.0	.74	2.7	-1.4	-3.8	.06	-129	-131	-17.2
8/3/2007	0:45	3.68	15.6	13.7	6.0	.73	2.6	-1.4	-3.8	.05	-129	-132	-17.2
8/3/2007	2:15	3.61	15.6	13.6	5.9	.75	2.6	-1.4	-3.8	.06	-129	-131	-17.2
8/3/2007	3:45	3.66	15.5	13.7	6.0	.73	2.7	-1.4	-3.8	.06	-129	-131	-17.2
8/3/2007	5:15	3.64	15.6	13.7	6.0	.70	2.7	-1.5	-3.8	.07	-129	-131	-17.2
8/3/2007	6:45	3.69	15.7	13.7	6.1	.73	2.7	-1.4	-3.8	.06	-129	-131	-17.2
8/3/2007	8:15	3.77	15.8	13.7	6.0	.73	2.7	-1.4	-3.9	.05	-129	-131	-17.3
8/3/2007	9:45	3.91	15.9	13.6	6.0	.73	2.7	-1.4	-3.8	.07	-129	-131	-17.2
8/3/2007	11:15	3.88	16.0	13.7	6.0	.75	2.7	-1.3	-3.8	.06	-129	-131	-17.2

[a] Parkhurst and Apello, 1999

[b] Delany and Lundeen, 1990

[c] Data for schwertmannite from Bigham and others, 1996

[d] Ball and Nordstrom, 1991

Table 8. Pearson product-moment correlation coefficients for selected constituents in Grape Creek, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007.

[Correlations greater than 0.70 or less than -0.70 in gray and bold; na, not attempted, non-linear relation; -, indicates redundant cell]

	Calcium	Magnesium	Potassium	Sodium	Sulfate	Chloride	Silica	Aluminum	Arsenic	Barium	Beryllium	Boron	Cadmium	Chromium	Cobalt	Copper
Calcium	-	0.49	0.63	0.57	-0.04	0.05	0.33	0.05	0.01	-0.01	-0.04	0.10	0.01	-0.01	-0.01	-0.10
Magnesium	-	-	**.77**	**.82**	-.11	.13	.00	.00	-.14	.17	-.05	.07	-.07	-.02	-.17	-.03
Potassium	-	-	-	.64	-.07	.16	.10	.04	-.09	.02	-.06	.12	.04	-.03	-.10	-.10
Sodium	-	-	-	-	.02	.15	.01	.00	-.07	.17	-.02	.08	.01	-.03	-.06	-.04
Sulfate	-	-	-	-	-	.00	-.03	-.19	.10	.00	.35	-.05	.37	-.04	.45	.00
Chloride	-	-	-	-	-	-	-.02	.00	-.13	.06	.00	.04	.00	-.12	.00	.00
Silica	-	-	-	-	-	-	-	.08	.11	-.23	-.06	.02	.00	.00	.00	-.21
Aluminum	-	-	-	-	-	-	-	-	.00	.00	-.25	.44	.01	.06	-.08	.00
Arsenic	-	-	-	-	-	-	-	-	-	.00	.04	-.03	.34	.16	.28	-.06
Barium	-	-	-	-	-	-	-	-	-	-	-.02	.02	.02	.00	.00	.01
Beryllium	-	-	-	-	-	-	-	-	-	-	-	-.19	.30	.00	.65	.02
Boron	-	-	-	-	-	-	-	-	-	-	-	-	.04	-.01	-.08	.00
Cadmium	-	-	-	-	-	-	-	-	-	-	-	-	-	.04	.56	.00
Chromium	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.02	-.03
Cobalt	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.00
Copper	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Iron	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Lead	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Manganese	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Nickel	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Selenium	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Strontium	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Thallium	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Vanadium	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Zinc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Uranium	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
pH	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temperature	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Specific conductance	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Dissolved oxygen	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Iron	Lead	Manganese	Nickel	Selenium	Strontium	Thallium	Vanadium	Zinc	Uranium	pH	Temperature	Specific conductance	Dissolved oxygen	Oxidation-reduction potential	Solar radiation
0.00	0.00	-0.07	0.00	0.00	-0.02	0.00	0.00	0.04	0.09	0.00	0.02	0.01	0.01	-0.05	0.02
-.16	.36	-.07	-.04	-.05	-.05	-.01	-.18	.02	.22	.20	-.03	.18	.19	.00	.15
-.04	.00	-.08	-.04	-.05	.04	-.01	-.08	.00	.10	.05	-.01	.04	.05	.00	.03
-.10	.01	-.02	-.03	.00	.00	.00	-.14	.00	.19	.12	.00	.00	.13	-.01	.10
.15	-.29	.37	.04	.49	.63	.03	.01	.00	-.17	.01	.04	.02	-.26	.00	.10
-.01	-.03	.00	.00	-.03	-.01	-.04	-.05	.02	.00	.10	-.04	.15	.05	-.01	.01
.14	.00	-.05	.00	-.01	-.04	.02	.16	.12	.02	-.30	.05	-.22	-.09	-.01	.01
-.05	.27	-.11	.11	-.16	-.11	.00	-.01	.53	.18	.00	-.04	-.02	.13	.00	.15
.23	.03	.15	.09	.15	.08	.36	.42	.06	.00	-.26	.06	-.12	-.12	-.03	-.04
-.29	.18	.00	.11	.00	.00	.06	-.25	-.03	.17	.44	-.05	.52	.34	-.01	.19
.03	-.09	**.73**	-.14	.51	.54	.00	.10	-.06	-.05	.00	.02	.01	-.06	.00	-.12
.00	.02	-.08	.04	-.04	-.03	.00	-.02	.60	.09	.00	.02	.01	.03	.00	.02
.04	.00	.42	.01	.39	.45	.30	.12	.01	-.03	.00	.01	.00	.00	-.01	-.06
.00	.07	.02	.09	.00	-.05	.09	.10	.00	.00	.00	-.01	-.02	.03	.01	.03
.10	-.06	**.77**	.00	**.72**	**.73**	.08	.20	.00	-.06	-.03	.07	.00	-.14	-.05	-.15
-.03	.01	.00	-.01	.00	.00	.00	-.04	-.02	.00	.08	-.04	.03	.03	.02	.00
-	-.34	.04	-.02	.03	.04	.05	**.73**	.06	.25	-.34	.18	-.17	**-.78**	.00	**-.78**
-	-	-.04	.11	-.07	-.08	.05	-.08	.00	.37	.04	-.09	.01	.48	-.04	**.70**
-	-	-	-.03	.62	.58	.07	.11	.00	-.02	.00	.04	.04	-.07	-.01	-.09
-	-	-	-	.00	-.01	.11	-.01	.03	.01	-.01	.01	.00	.04	-.13	.11
-	-	-	-	-	**.71**	.05	.04	.00	-.02	-.02	.10	.04	-.11	-.13	-.17
-	-	-	-	-	-	.04	.04	.00	-.03	.00	.03	.08	-.08	-.06	-.10
-	-	-	-	-	-	-	.07	.04	-.17	.00	.00	.00	-.16	.08	.00
-	-	-	-	-	-	-	-	.03	.12	-.29	.04	-.25	-.28	.00	.52
-	-	-	-	-	-	-	-	-	.00	-.06	.00	-.05	-.03	.00	.02
-	-	-	-	-	-	-	-	-	-	.09	-.02	.12	.38	-.02	.59
-	-	-	-	-	-	-	-	-	-	-	-.50	-.59	.49	.11	-.04
-	-	-	-	-	-	-	-	-	-	-	-	-.08	-.43	-.27	na
-	-	-	-	-	-	-	-	-	-	-	-	-	.26	.00	.55
-	-	-	-	-	-	-	-	-	-	-	-	-	-	.00	na

Table 9. Summary of pH, temperature, and mineral saturation indexes computed for samples from Grape Creek, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007.

[PHREEQC, pH-redox-equilibrium-equations in C code; CDT, Central Daylight Time; WATEQ4F, Water equilibrium model, FORTRAN code; (ss) solid solution; (a) amorphous; see appendix 4 for mineral formulas]

Date and CDT (month/day/ year hour:minute)	pH (standard units)	Water temperature (degrees Celsius)	Saturation indexes calculated by PHREEQC[a]												
			Mineral in Lawrence Livermore National Laboratory database[b]	Minerals in the WATE4F database[c]											
			$Fe(OH)_2$	Alunite	Barite	Cuprous Ferrite	$Fe(OH)_3$(a)	Goethite	Gypsum	Hematite	Jarosite (ss)	Jurbanite	Silicagel	SiO_2(a)	Schwertmannite[d]
8/1/07 11:15	3.46	22.1	-15.9	0.75	0.25	-5.04	0.65	6.44	-0.05	14.9	7.90	0.21	.12	-.20	10.3
8/1/07 12:15	3.43	22.9	-15.9	.68	.13	-5.06	.53	6.34	-.09	14.7	7.56	.19	.10	-.22	9.4
8/1/07 13:15	3.46	24.3	-15.9	.87	.20	-4.43	.48	6.35	-.10	14.7	7.32	.15	.03	-.28	8.9
8/1/07 14:15	3.23	25.5	-15.8	-.17	.14	-5.63	-.08	5.82	-.11	13.7	6.37	-.01	.04	-.27	5.2
8/1/07 15:15	3.24	26.5	-16.1	-.11	.07	-5.22	-.06	5.89	-.09	13.8	6.43	-.05	.05	-.26	5.4
8/1/07 16:15	3.15	27.0	-16.0	-.61	.07	-5.77	-.33	5.63	-.06	13.3	5.93	-.15	.03	-.27	3.5
8/1/07 17:15	3.13	27.0	-16.1	-.69	.11	-5.64	-.29	5.67	-.10	13.4	6.06	-.14	.03	-.27	3.9
8/1/07 18:15	3.16	26.8	-16.1	-.60	.14	-5.70	-.24	5.71	-.10	13.4	6.13	-.14	.03	-.27	4.2
8/1/07 19:15	3.28	26.1	-16.1	.13	.17	-5.15	.17	6.10	-.10	14.2	6.99	.02	.04	-.27	7.1
8/1/07 20:15	3.33	25.7	-15.8	.33	.11	-6.27	.35	6.26	-.10	14.5	7.37	.05	.05	-.25	8.3
8/1/07 21:15	3.35	25.3	-15.7	.42	.08	-5.35	-.19	5.71	-.10	13.4	5.66	.07	.04	-.26	4.0
8/1/07 22:15	3.33	24.7	-15.7	.14	.05	-4.43	.39	6.27	-.08	14.6	7.52	.03	.07	-.24	8.7
8/1/07 23:15	3.3	24.1	-16.3	.02	.09	-5.26	.33	6.19	-.05	14.4	7.47	.05	.09	-.22	8.4
8/2/07 0:15	3.35	23.3	-15.8	-.02	.07	-5.00	.46	6.29	-.08	14.6	7.65	.02	.08	-.23	9.2
8/2/07 1:15	3.31	23.0	-15.9	-.15	.10	-6.53	.37	6.19	-.08	14.4	7.53	.02	.09	-.22	8.6
8/2/07 2:15	3.28	22.2	-15.9	-.49	.12	-6.69	.34	6.13	-.09	14.2	7.50	-.02	.09	-.23	8.4
8/2/07 3:15	3.28	22.2	-16.0	-.49	.05	-5.06	.31	6.10	-.09	14.2	7.41	-.02	.10	-.21	8.2
8/2/07 4:15	3.31	21.7	-16.1	-.22	.10	-6.59	.41	6.18	-.07	14.3	7.64	.06	.11	-.21	8.9
8/2/07 5:15	3.35	21.3	-16.2	-.09	.10	-6.42	.52	6.28	-.08	14.6	7.83	.08	.11	-.21	9.7
8/2/07 6:15	3.29	21.3	-16.1	-.38	.07	-6.57	.35	6.11	-.06	14.2	7.54	.04	.11	-.20	8.6
8/2/07 7:15	3.34	20.9	-16.1	-.09	.08	-6.39	.46	6.21	-.06	14.4	7.72	.10	.12	-.20	9.3
8/2/07 8:15	3.38	21.1	-16.1	.18	.08	-5.32	.53	6.28	-.04	14.5	7.81	.15	.12	-.20	9.7

Table 9. Summary of pH, temperature, and mineral saturation indexes computed for samples from Grape Creek, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. —Continued

[PHREEQC, pH-redox-equilibrium-equations in C code; CDT, Central Daylight Time; WATEQ4F, Water equilibrium model, FORTRAN code; (ss) solid solution; (a) amorphous; see appendix 4 for mineral formulas]

Date and CDT (month/day/ year hour:minute)	pH (standard units)	Water temperature (degrees Celsius)	Saturation indexes calculated by PHREEQC[a]												
			Mineral in Lawrence Livermore National Laboratory database[b]	Minerals in the WATE4F database[c]											
			$Fe(OH)_2$	Alunite	Barite	Cuprous Ferrite	$Fe(OH)_3$(a)	Goethite	Gypsum	Hematite	Jarosite (ss)	Jurbanite	Silicagel	SiO_2(a)	Schwertmannite[d]
8/2/07 9:15	3.31	21.4	-16.0	-0.19	0.13	-4.89	0.29	6.06	-0.10	14.1	7.25	0.08	0.11	-0.21	8.0
8/2/07 10:15	3.3	21.9	-16.0	-.26	-.06	-4.95	.26	6.04	-.09	14.1	7.17	.05	.09	-.22	7.7
8/2/07 11:15	3.26	22.5	-16.0	-.35	.11	-5.61	.12	5.92	-.08	13.8	6.90	.02	.10	-.21	6.7
8/2/07 12:15	3.23	23.5	-16.1	-.44	.10	-5.84	-.03	5.81	-.04	13.6	6.62	-.02	.11	-.20	5.7
8/2/07 13:15	3.22	24.6	-16.1	-.39	.17	-5.85	-.10	5.78	-.09	13.6	6.38	-.04	.07	-.24	5.2
8/2/07 14:15	3.14	25.8	-16.1	-.72	.11	-6.04	-.34	5.57	-.11	13.2	5.86	-.12	.05	-.25	3.4
8/2/07 15:15	3.1	26.8	-16.2	-.92	.11	-6.23	-.40	5.55	-.12	13.1	5.81	-.18	.04	-.26	3.1
8/2/07 16:15	3.1	27.2	-16.2	-.80	.11	-6.17	-.45	5.52	-.07	13.1	5.73	-.17	.03	-.27	2.8
8/2/07 17:15	3.08	27.3	-16.2	-1.02	.00	-5.96	-.51	5.46	-.11	12.9	5.54	-.22	.03	-.27	2.3
8/2/07 18:15	3.08	27.1	-16.1	-.95	.09	-6.02	-.47	5.49	-.09	13.0	5.71	-.19	.04	-.26	2.7
8/2/07 19:15	3.06	26.6	-16.1	-1.14	.04	-5.56	-.45	5.50	-.14	13.0	5.78	-.21	.01	-.29	2.9
8/2/07 20:15	3.06	26.7	-16.2	-1.14	.07	-7.47	-.47	5.48	-.09	13.0	5.78	-.21	.04	-.26	2.7
8/2/07 21:15	3.21	25.7	-16.1	-.50	.03	-5.46	-.01	5.90	-.08	13.8	6.68	-.11	.06	-.24	5.9
8/2/07 22:15	3.18	25.0	-16.2	-.67	.04	-4.89	-.01	5.89	-.12	13.8	6.75	-.10	.05	-.26	6.0
8/2/07 23:15	3.31	24.7	-16.2	.09	-2.11	-6.38	.28	6.16	-.11	14.3	7.19	.03	.05	-.26	7.8
8/3/07 0:15	3.22	24.0	-15.9	-.60	.02	-5.37	.08	5.93	-.11	13.9	6.87	-.08	.07	-.23	6.5
8/3/07 1:15	3.22	23.5	-16.0	-.50	.03	-6.80	.10	5.93	-.07	13.9	7.00	-.03	.10	-.21	6.7
8/3/07 2:15	3.25	22.9	-15.8	-.44	-.07	-6.71	.18	6.00	-.07	14.0	7.17	-.02	.11	-.21	7.3
8/3/07 3:15	3.29	22.5	-16.0	-.21	.08	-6.54	.33	6.13	-.09	14.3	7.45	.04	.09	-.22	8.3
8/3/07 4:15	3.36	22.1	-16.0	.09	.05	-4.88	.51	6.29	-.10	14.6	7.73	.10	.10	-.21	9.5
8/3/07 5:15	3.29	21.8	-16.0	-.38	.09	-5.18	.36	6.13	-.09	14.3	7.52	.02	.11	-.20	8.6
8/3/07 6:15	3.3	21.4	-16.0	-.44	.03	-6.50	.38	6.14	-.10	14.3	7.56	.01	.10	-.22	8.7

Table 9. Summary of pH, temperature, and mineral saturation indexes computed for samples from Grape Creek, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. —Continued

[PHREEQC, pH-redox-equilibrium-equations in C code; CDT, Central Daylight Time; WATEQ4F, Water equilibrium model, FORTRAN code; (ss) solid solution; (a) amorphous; see appendix 4 for mineral formulas]

Date and CDT (month/day/year hour:minute)	pH (standard units)	Water temperature (degrees Celsius)	Saturation indexes calculated by PHREEQC[a]												
			Mineral in Lawrence Livermore National Laboratory database[b]	Minerals in the WATE4F database[c]											
			$Fe(OH)_2$	Alunite	Barite	Cuprous Ferrite	$Fe(OH)_3$(a)	Goethite	Gypsum	Hematite	Jarosite (ss)	Jurbanite	Silicagel	SiO_2(a)	Schwertmannite[d]
8/3/07 7:15	3.31	21.3	-15.9	-0.25	-0.04	-5.11	0.40	6.16	-0.08	14.3	7.61	0.07	0.11	-0.20	8.9
8/3/07 8:15	3.3	21.6	-16.0	-.35	.06	-6.55	.31	6.08	-.10	14.2	7.34	.03	.11	-.20	8.2
8/3/07 9:15	3.31	21.9	-16.0	-.19	-.02	-5.16	.28	6.06	-.08	14.1	7.21	.06	.11	-.20	7.8
8/3/07 10:15	3.24	22.4	-16.0	-.43	.08	-5.65	.05	5.84	-.09	13.7	6.75	.02	.09	-.22	6.2
8/3/07 11:15	3.19	23.0	-16.0	-.67	.00	-5.70	-.08	5.74	-.09	13.5	6.55	-.04	.10	-.21	5.4

[a] Parkhurst and Apello, 1999

[b] Delany and Lundeen, 1990

[c] Ball and Nordstrom, 1991

[d] Data for schwertmannite from Bigham and others, 1996

Appendixes 1–4

Appendix 1. Water-quality data from well MW3, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007.

[M/D/Y, month/day/year; HH:MM, hour:minute; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; e, estimated concentration; –, no data; duplicate samples in bold]

Date and time of sample collection (M/D/Y HH:MM)	Calcium (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Sulfate[1] (mg/L)	Chloride (mg/L)	Silica (mg/L)	Aluminum (µg/L)	Antimony (µg/L)	Arsenic (µg/L)	Barium (µg/L)	Beryllium (µg/L)	Boron (µg/L)	Cadmium (µg/L)	Chromium (µg/L)	Cobalt (µg/L)
8/1/07 12:45	530	30	4.4	38	2,100	5.8	110	91,000	<0.12	1.3	5	15	3,900	59	2.4	27
8/1/07 14:15	520	30	4.6	38	2,000	3.7	110	87,000	<.12	1.3	5.1	13	3,700	65	2.4	28
8/1/07 15:45	520	30	4.5	38	2,100	3.7	110	91,400	<.12	1.3	6	12	3,900	60	2.4	27
8/1/07 17:15	490	29	4.3	37	2,000	3.9	110	91,400	<.12	1.2	6	8.7	4,000	62	2.4	25
8/1/07 18:45	510	30	4.4	38	2,000	4.2	110	91,800	<.12	1.2	6	8.9	4,100	67	2.3	25
8/1/07 20:15	490	28	4.4	36	1,900	4.2	100	82,800	<.12	1.2	5	9.7	3,700	62	2.5	27
8/1/07 21:45	510	30	4.4	38	2,100	4.1	110	96,300	<.12	1.0	5	9.6	4,300	61	2.2	25
8/1/07 23:15	520	29	4.6	36	2,000	3.9	110	93,200	<.12	1.0	5	9.2	3,900	65	2.3	24
8/2/07 0:45	520	30	4.6	39	2,100	4.1	110	91,000	<.12	1.1	5	9.7	4,000	59	2.3	25
8/2/07 2:15	540	31	4.8	40	2,100	4.3	110	92,200	<.12	.96	6	9.1	4,100	66	2.4	26
8/2/07 3:45	**560**	**32**	**4.9**	**41**	2,100	**3.9**	**120**	**88,600**	**<.12**	**1.0**	**5**	**10**	**3,900**	**58**	**2.2**	**24**
8/2/07 3:46	**500**	**29**	**4.4**	**37**	2,000	**4.1**	**110**	**87,900**	**<.12**	**1.0**	**5.5**	**9.6**	**3,900**	**61**	**2.3**	**25**
8/2/07 5:15	490	29	4.3	36	2,000	3.9	110	88,700	<.12	.96	6	9.1	3,900	64	2.2	24
8/2/07 6:45	500	30	4.4	37	2,000	3.9	110	90,000	<.12	1.2	6	8.6	3,800	64	2.4	25
8/2/07 8:15	500	29	4.4	37	2,000	3.9	110	91,800	<.12	1.0	6	8.2	4,100	67	2.4	26
8/2/07 9:45	**520**	**30**	**4.6**	**38**	2,000	**4.2**	**110**	**92,900**	**<.12**	**1.0**	**6**	**10**	**4,100**	**64**	**2.3**	**25**
8/2/07 9:46	**520**	**30**	**4.5**	**39**	2,000	**4.2**	**110**	**89,500**	**<.12**	**1.0**	**5.3**	**9.7**	**3,900**	**61**	**2.3**	**25**
8/2/07 11:15	510	30	4.5	38	2,000	4.0	110	82,400	<.12	.98	6	9.0	3,600	67	2.4	26
8/2/07 12:45	500	29	4.5	37	2,000	4.1	110	88,500	<.12	1.0	6	10	3,800	58	2.3	24
8/2/07 14:15	520	30	4.5	38	2,000	4.1	110	85,100	<.12	1.2	6	9.1	3,600	65	2.4	26
8/2/07 15:45	550	31	4.8	38	2,100	4.2	110	89,000	<.12	1.1	6	11	3,900	69	2.6	28
8/2/07 17:15	520	30	4.6	39	2,000	4.5	110	90,100	<.60	1.2	4	19	3,800	70	2.5	30
8/2/07 18:45	510	30	4.6	38	2,000	4.1	110	88,000	<.60	1.2	4	20	3,900	73	1.7	30

Appendix 1. Water-quality data from well MW3, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. —Continued

[M/D/Y, month/day/year; HH:MM, hour:minute; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; e, estimated concentration; –, no data; duplicate samples in bold]

Date and time of sample collection (M/D/Y HH:MM)	Calcium (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Sulfate[1] (mg/L)	Chloride (mg/L)	Silica (mg/L)	Aluminum (µg/L)	Antimony (µg/L)	Arsenic (µg/L)	Barium (µg/L)	Beryllium (µg/L)	Boron (µg/L)	Cadmium (µg/L)	Chromium (µg/L)	Cobalt (µg/L)
8/2/07 20:15	540	31	4.8	40	2,100	4.6	110	94,200	<0.60	1.2	5	18	4,000	71	2.4	29
8/2/07 21:45	530	30	4.8	39	2,000	4.4	110	85,100	<.60	e1.0	4	19	3,700	67	2.3	28
8/2/07 23:15	520	30	4.6	39	2,100	4.4	110	90,400	<.60	1.3	5	20	4,000	68	2.3	29
8/3/07 0:45	510	29	4.7	37	2,000	4.8	110	88,400	<.60	1.2	5	18	3,700	66	2.4	27
8/3/07 2:15	**530**	**30**	**4.7**	**39**	2,100	**4.5**	**110**	**93,000**	**<.12**	**1.0**	**5**	**8.5**	**4,000**	**76**	**2.3**	**26**
8/3/07 2:16	**530**	**30**	**4.8**	**39**	2,000	**4.3**	**110**	**87,300**	**<.12**	**.80**	**5.5**	**9.3**	**3,800**	**78**	**2.1**	**25**
8/3/07 3:45	510	30	4.6	38	2,000	4.4	110	87,400	<.12	.96	6	7.9	3,600	73	1.9	24
8/3/07 5:15	530	30	4.8	39	2,000	4.4	110	82,000	<.60	1.2	4	19	3,600	69	2.3	28
8/3/07 6:45	520	31	4.8	38	2,100	4.4	110	88,900	<.60	e1.0	4	19	3,900	66	2.3	28
8/3/07 8:15	500	29	4.8	37	2,000	3.9	110	88,700	.54	1.0	6	8.4	3,800	77	2.1	25
8/3/07 9:45	**520**	**30**	**4.8**	**38**	2,000	**4.4**	**110**	**88,400**	**<.12**	**.94**	**6**	**8.0**	**3,800**	**72**	**1.9**	**24**
8/3/07 9:46	**510**	**30**	**4.7**	**38**	2,000	**4.0**	**110**	**84,900**	**<.12**	**1.1**	**4.6**	**20**	**3,800**	**76**	**2.3**	**29**
8/3/07 11:15	510	29	4.7	38	2,000	4.4	110	92,700	<.12	.96	6	7.6	4,000	74	1.9	24

Appendix 1. Water-quality data from well MW3, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. —Continued

[M/D/Y, month/day/year; HH:MM, hour:minute; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; e, estimated concentration; –, no data; duplicate samples in bold]

Date and time of sample collection (M/D/Y HH:MM)	Copper (µg/L)	Iron (µg/L)	Lead (µg/L)	Lithium (µg/L)	Manganese (µg/L)	Molybdenum (µg/L)	Nickel (µg/L)	Selenium (µg/L)	Silver (µg/L)	Strontium (µg/L)	Thallium (µg/L)	Uranium (µg/L)	Vanadium (µg/L)	Zinc (µg/L)	Nitrite plus nitrate, as nitrogen (mg/L)	Nitrite, as nitrogen (mg/L)
8/1/07 12:45	11	13,400	1.2	550	3,400	<0.2	110	0.74	<0.2	960	<0.08	3.1	0.34	44,000	<0.06	<0.002
8/1/07 14:15	12	12,100	1.1	530	3,500	<.2	110	.70	<.2	1,100	<.08	3.3	.24	41,900	<.06	<.002
8/1/07 15:45	11	13,700	1.2	550	3,400	<.2	110	.84	<.2	970	<.08	3.2	.28	43,900	<.06	<e.002
8/1/07 17:15	11	12,400	1.2	240	3,000	<.2	100	.56	<.2	890	<.08	3.1	.18	44,100	<.06	.001
8/1/07 18:45	12	12,100	1.2	240	3,000	<.2	100	.56	<.2	910	e.04	3.3	.14	44,200	<.06	<.002
8/1/07 20:15	14	10,700	1.1	260	3,300	<.2	110	.62	<.2	880	e.04	3.1	.18	40,700	<.06	<.002
8/1/07 21:45	12	11,200	1.1	150	2,900	<.2	100	.54	<.2	870	<.08	3.1	.12	46,800	<.06	<.002
8/1/07 23:15	12	12,200	1.1	160	2,800	<.2	96	.56	<.2	750	<.08	3.1	.16	44,400	<.06	<.002
8/2/07 0:45	14	11,000	1.0	150	2,900	<.2	100	.54	<.2	850	e.04	2.9	.16	44,400	<.06	<.002
8/2/07 2:15	14	12,000	1.2	140	3,000	<.2	100	.54	<.2	920	e.04	3.2	.14	43,800	<.06	<.002
8/2/07 3:45	**12**	**12,400**	**1.1**	**140**	**2,800**	**<.2**	**97**	**.54**	**<.2**	**770**	**<.08**	**2.8**	**.12**	**43,100**	**<.06**	**<.002**
8/2/07 3:46	**13**	**11,000**	**1.1**	**140**	**2,800**	**<.2**	**100**	**.60**	**<.2**	**840**	**<.08**	**3.0**	**.12**	**41,900**	**<.06**	**<.002**
8/2/07 5:15	14	10,800	1.3	120	2,800	<.2	98	.52	<.2	860	<.08	3.1	.12	42,700	<.06	<.002
8/2/07 6:45	12	12,900	1.3	150	2,900	<.2	99	.54	<.2	910	<.08	3.2	.14	42,500	<.06	<.002
8/2/07 8:15	14	11,400	1.2	120	2,900	<.2	110	.60	<.2	920	e.04	3.2	.12	44,000	<.06	<e.002
8/2/07 9:45	**14**	**11,300**	**1.1**	**120**	**2,800**	**<.2**	**100**	**.56**	**<.2**	**860**	**e.04**	**3.1**	**.12**	**44,900**	**<.06**	**.001**
8/2/07 9:46	**13**	**11,100**	**1.1**	**140**	**2,900**	**<.2**	**99**	**.50**	**<.2**	**830**	**<.08**	**3.1**	**.14**	**42,600**	**<.06**	**<.002**
8/2/07 11:15	14	11,500	1.1	130	3,000	<.2	100	.54	<.2	920	<.08	3.1	.14	39,500	<.06	<e.002
8/2/07 12:45	13	11,600	1.0	130	2,800	<.2	98	.60	<.2	810	<.08	3.0	.14	42,000	<.06	.001
8/2/07 14:15	14	11,500	1.1	160	3,100	<.2	100	.62	<.2	910	<.08	3.1	.14	39,800	<.06	<.002
8/2/07 15:45	14	11,900	1.1	180	3,400	<.2	110	.60	<.2	780	e.04	3.2	.16	44,200	<.06	<.002
8/2/07 17:15	17	10,900	e1.1	140	3,600	<1.2	120	e.60	<1.0	1,100	<.40	3.3	<.40	39,700	<.06	<.002
8/2/07 18:45	16	11,600	e1.0	530	3,700	<1.2	120	e.70	<1.0	1,100	<.40	3.4	<.40	44,500	<.06	<.002

Appendix 1. Water-quality data from well MW3, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. —Continued

[M/D/Y, month/day/year; HH:MM, hour:minute; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; e, estimated concentration; –, no data; duplicate samples in bold]

Date and time of sample collection (M/D/Y HH:MM)	Copper (µg/L)	Iron (µg/L)	Lead (µg/L)	Lithium (µg/L)	Manganese (µg/L)	Molyb-denum (µg/L)	Nickel (µg/L)	Selenium (µg/L)	Silver (µg/L)	Strontium (µg/L)	Thallium (µg/L)	Uranium (µg/L)	Vanadium (µg/L)	Zinc (µg/L)	Nitrite plus nitrate, as nitrogen (mg/L)	Nitrite, as nitrogen (mg/L)
8/2/07 20:15	16	12,200	e1.1	500	3,600	<1.2	110	e0.50	<1.0	1,100	<0.40	3.3	<0.40	46,400	<0.06	<0.002
8/2/07 21:45	14	11,500	e1.0	500	3,400	<1.2	110	e.50	<1.0	1,100	<.40	3.1	<.40	43,500	<.06	<.002
8/2/07 23:15	15	11,100	e1.1	520	3,600	<1.2	110	e.60	<1.0	1,100	<.40	3.2	.20	45,400	<.06	<.002
8/3/07 0:45	17	11,100	1.8	460	3,400	<1.2	110	e.70	<1.0	950	<.40	3.0	<.40	40,000	<.06	<.002
8/3/07 2:15	**14**	**10,700**	**1.5**	**670**	**3,000**	**<.2**	**100**	**.54**	**<.2**	**1,100**	**<.40**	**3.9**	**.10**	**45,800**	**<.06**	**<.002**
8/3/07 2:16	**14**	**10,800**	**1.5**	**640**	**2,600**	**<.2**	**98**	**.50**	**<.2**	**1,100**	**<.40**	**4.0**	**.12**	**41,800**	**<.06**	**<.002**
8/3/07 3:45	13	11,100	1.4	720	2,600	<.2	93	.46	<.2	1,000	<.40	3.8	.10	41,300	<.06	<.002
8/3/07 5:15	16	11,300	1.3	500	3,400	<1.2	110	e.60	<1.0	1,100	<.40	3.2	<.40	41,000	<.06	<.002
8/3/07 6:45	16	11,600	1.3	510	3,500	<1.2	110	e.60	<1.0	1,000	<.40	3.2	<.40	44,000	<.06	<.002
8/3/07 8:15	17	11,400	1.2	780	2,700	<.2	99	.50	<.2	1,100	<.40	3.9	.12	42,100	<.06	<e.002
8/3/07 9:45	**13**	**11,000**	**1.3**	**700**	**2,600**	**<.2**	**94**	**.44**	**<.2**	**990**	**<.40**	**3.7**	**.12**	**42,600**	**<.06**	**.001**
8/3/07 9:46	**16**	**10,800**	**1.2**	**520**	**3,600**	**<.2**	**110**	**e.60**	**<.2**	**1,200**	**<.40**	**3.3**	**<.40**	**42,900**	**<.06**	**<.002**
8/3/07 11:15	12	11,000	1.3	700	2,600	<.2	93	.48	<.2	1,000	<.40	3.7	.10	44,700	<.06	<.002

Appendix 1. Water-quality data from well MW3, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. —Continued

[M/D/Y, month/day/year; HH:MM, hour:minute; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; e, estimated concentration; –, no data; duplicate samples in bold]

Date and time of sample collection (M/D/Y HH:MM)	Temperature (degrees Celsius)	Specific conductance (microsiemens per centimeter)	Dissolved oxygen (mg/L)	pH (standard units)	Oxidation reduction (millivolts)
8/1/07 12:45	15.97	2,760	1.0	3.85	340
8/1/07 14:15	16.27	2,760	1.1	4.22	350
8/1/07 15:45	16.26	2,770	1.5	4.06	340
8/1/07 17:15	16.02	2,760	1.0	3.95	350
8/1/07 18:45	15.99	2,770	1.0	3.77	360
8/1/07 20:15	15.74	2,760	1.0	3.74	360
8/1/07 21:45	15.57	2,760	1.0	3.71	370
8/1/07 23:15	15.54	2,770	3.6	3.72	370
8/2/07 0:45	15.58	2,760	.8	3.70	370
8/2/07 2:15	15.51	2,770	1.3	3.70	–
8/2/07 3:45	15.47	2,770	1.3	3.68	–
8/2/07 5:15	15.45	2,770	1.7	3.68	–
8/2/07 6:45	15.63	2,780	1.5	3.67	370
8/2/07 8:15	15.88	2,780	1.2	3.81	370
8/2/07 9:45	16.02	2,770	1.1	3.88	370
8/2/07 11:15	15.99	2,780	1.1	4.04	370
8/2/07 12:45	15.98	2,780	1.0	3.81	370
8/2/07 14:15	16.66	2,770	1.0	3.78	370
8/2/07 15:45	16.20	2,780	1.1	3.96	360
8/2/07 17:15	16.18	2,760	.9	3.72	380
8/2/07 18:45	15.91	2,760	1.1	3.74	380
8/2/07 20:15	15.71	2,780	.8	3.71	–
8/2/07 21:45	15.74	2,770	1.1	3.68	380
8/2/07 23:15	15.61	2,760	1.0	3.61	380
8/3/07 0:45	15.55	2,770	1.9	3.68	380
8/3/07 2:15	15.61	2,760	1.0	3.61	380
8/3/07 3:45	15.53	2,770	.9	3.66	380
8/3/07 5:15	15.61	2,760	1.1	3.64	380
8/3/07 6:45	15.65	2,770	1.0	3.69	380
8/3/07 8:15	15.80	2,770	1.0	3.77	370
8/3/07 9:45	15.93	2,750	1.1	3.91	380
8/3/07 11:15	16.02	2,770	1.1	3.88	370

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[1] Concentrations of sulfate based on calculation of electroneutrality of sample solution.

Appendix 2. Water-quality data from Grape Creek at streamgage SW1, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007.

[M/D/Y, month/day/year; HH:MM, hour:minute; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; e, estimated concentration; –, no data; duplicate samples in bold]

Date and time of sample collection (M/D/Y HH:MM)	Calcium (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Sulfate[1] (mg/L)	Chloride (mg/L)	Silica (mg/L)	Aluminum (µg/L)	Antimony (µg/L)	Arsenic (µg/L)
8/1/07 11:15	**510**	**35**	**7.4**	**38**	**2,100**	**5.4**	**69**	**48,300**	**<0.12**	**4.0**
8/1/07 11:16	**510**	**35**	**7.5**	**37**	**2,000**	**6.0**	**72**	**49,500**	**<.12**	**4.5**
8/1/07 12:15	480	32	6.8	35	1,900	4.3	67	49,000	<.12	4.3
8/1/07 13:15	470	36	7.2	38	1,800	5.9	60	42,700	<.60	3.3
8/1/07 14:15	470	33	7.0	36	1,900	6.5	63	51,100	<.06	3.4
8/1/07 15:15	490	35	7.4	37	1,900	5.8	66	46,200	<.60	3.4
8/1/07 16:15	520	37	7.6	40	2,000	5.9	65	45,900	<.60	2.8
8/1/07 17:15	470	33	6.9	36	2,000	5.9	65	48,200	<.60	4.1
8/1/07 18:15	480	34	7.2	37	2,000	6.3	64	45,400	<.60	4.5
8/1/07 19:15	470	33	7.0	36	2,000	6.1	63	49,000	<.60	3.9
8/1/07 20:15	**480**	**33**	**7.1**	**36**	**2,000**	**6.4**	**65**	**46,800**	**<.60**	**3.5**
8/1/07 20:16	**460**	**32**	**7.0**	**35**	**2,000**	**6.3**	**65**	**48,000**	**<.60**	**4.4**
8/1/07 21:15	480	33	7.2	36	1,800	5.8	63	45,700	<.60	2.3
8/1/07 22:15	490	33	7.0	36	2,000	6.1	66	44,600	<.60	3.6
8/1/07 23:15	520	35	7.5	36	2,200	6.1	68	49,100	<.60	3.2
8/2/07 0:15	490	33	7.1	36	2,000	6.5	65	40,200	<.60	3.3
8/2/07 1:15	480	33	7.2	36	2,000	6.3	66	44,600	<.60	3.9
8/2/07 2:15	470	32	6.9	35	2,000	6.4	65	42,800	<.60	4.5
8/2/07 3:15	480	32	7.0	35	2,000	5.6	66	42,500	<.60	4.5
8/2/07 4:15	500	33	7.1	36	2,100	6.3	67	47,900	<.60	4.3
8/2/07 5:15	480	32	6.9	35	2,000	6.1	67	45,500	<.60	4.3
8/2/07 6:15	500	32	7.0	36	2,100	5.9	67	48,200	<.60	4.5
8/2/07 7:15	**500**	**33**	**7.2**	**36**	**2,100**	**6.2**	**67**	**48,800**	**<.60**	**5.2**
8/2/07 7:16	**480**	**32**	**7.1**	**36**	**2,000**	**6.0**	**65**	**45,500**	**<.60**	**5.3**
8/2/07 8:15	520	34	7.4	36	2,100	5.8	68	49,500	<.60	4.0
8/2/07 9:15	470	32	6.8	35	1,900	5.4	66	49,700	<.12	4.2
8/2/07 10:15	480	31	6.6	34	2,000	4.6	65	47,900	<.60	3.3

Appendix 2. Water-quality data from Grape Creek at streamgage SW1, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007.—Continued

[M/D/Y, month/day/year; HH:MM, hour:minute; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; e, estimated concentration; –, no data; duplicate samples in bold]

Date and time of sample collection (M/D/Y HH:MM)	Calcium (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Sulfate[1] (mg/L)	Chloride (mg/L)	Silica (mg/L)	Aluminum (µg/L)	Antimony (µg/L)	Arsenic (µg/L)
8/2/07 11:15	480	32	7.2	35	2,000	5.9	67	49,600	<0.12	4.3
8/2/07 12:15	530	35	7.6	38	2,100	5.9	71	49,000	<.12	4.1
8/2/07 13:15	480	35	7.1	37	2,000	6.1	66	48,500	<.12	3.7
8/2/07 14:15	470	33	7.1	35	1,900	5.7	65	49,100	<.12	3.2
8/2/07 15:15	460	32	6.8	35	1,900	5.7	65	47,100	<.12	3.6
8/2/07 16:15	510	35	7.4	37	2,000	5.8	64	49,300	<.12	3.6
8/2/07 17:15	470	34	7.1	35	1,900	6.7	64	44,900	<.60	2.7
8/2/07 18:15	490	35	7.3	37	2,000	6.3	65	48,600	<.60	3.6
8/2/07 19:15	440	32	6.8	34	1,900	6.7	61	48,000	<.60	2.9
8/2/07 20:15	490	35	7.3	38	2,000	5.0	65	48,100	<.60	3.7
8/2/07 21:15	500	34	7.3	37	2,000	6.6	67	42,600	<.60	3.1
8/2/07 22:15	450	31	6.7	34	2,000	4.5	63	46,200	<.60	4.0
8/2/07 23:15	470	34	7.1	36	1,900	4.9	63	45,300	<.60	4.2
8/3/07 0:15	460	32	6.7	34	1,900	4.7	66	43,900	<.60	4.1
8/3/07 1:15	490	34	7.5	37	2,100	4.6	69	49,400	<.60	3.8
8/3/07 2:15	**490**	**35**	**7.6**	**36**	**2,100**	**6.4**	**69**	**46,800**	**<.60**	**3.2**
8/3/07 2:16	**470**	**31**	**6.7**	**34**	**2,100**	**4.9**	**66**	**43,500**	**<.60**	**4.5**
8/3/07 3:15	470	32	7.2	35	2,000	4.7	66	48,700	<.60	3.9
8/3/07 4:15	460	31	6.7	34	2,000	4.5	66	46,800	<.60	4.3
8/3/07 5:15	470	32	6.8	34	2,000	4.6	68	46,000	<.60	5.2
8/3/07 6:15	460	32	6.9	34	2,000	4.5	65	43,100	<.60	4.1
8/3/07 7:15	**480**	**33**	**7.1**	**35**	**2,000**	**6.2**	**67**	**48,200**	**<.60**	**2.9**
8/3/07 7:16	**490**	**33**	**7.3**	**36**	**2,100**	**6.1**	**67**	**48,000**	**<.60**	**3.8**
8/3/07 8:15	460	31	6.8	34	1,900	4.5	68	45,200	<.60	4.8
8/3/07 9:15	480	32	6.9	36	2,000	5.7	68	47,400	<.60	3.3
8/3/07 10:15	470	33	7.1	35	2,000	5.7	66	51,600	<.12	4.6
8/3/07 11:15	480	34	7.3	35	2,000	5.9	68	51,100	<.60	3.5

Appendix 2. Water-quality data from Grape Creek at streamgage SW1, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007.—Continued

[M/D/Y, month/day/year; HH:MM, hour:minute; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; e, estimated concentration; –, no data; duplicate samples in bold]

Date and time of sample collection (M/D/Y HH:MM)	Barium (µg/L)	Beryllium (µg/L)	Boron (µg/L)	Cadmium (µg/L)	Chromium (µg/L)	Cobalt (µg/L)	Copper (µg/L)	Iron (µg/L)	Lead (µg/L)	Lithium (µg/L)
8/1/07 11:15	**15**	**11**	**3,600**	**19**	**0.60**	**57**	**1.0**	**121,000**	**3.0**	**780**
8/1/07 11:16	**15**	**11**	**3,400**	**19**	**.60**	**58**	**1.0**	**119,000**	**3.0**	**640**
8/1/07 12:15	16	e10	3,500	19	.56	55	1.2	106,000	3.1	640
8/1/07 13:15	20	15	3,300	19	<1.2	53	e3.4	82,600	3.0	660
8/1/07 14:15	18	7.9	3,500	18	.44	46	2.1	91,600	3.2	680
8/1/07 15:15	16	17	3,400	21	e.60	56	e3.8	95,700	3.0	720
8/1/07 16:15	16	15	3,500	19	<1.2	52	e2.9	92,500	2.8	640
8/1/07 17:15	18	18	3,500	26	e.60	69	e3.7	112,000	3.0	740
8/1/07 18:15	19	17	3,300	23	e.60	67	e2.6	103,000	2.9	700
8/1/07 19:15	18	16	3,500	22	e.60	68	e2.3	129,000	2.4	640
8/1/07 20:15	**17**	**13**	**3,500**	**21**	**e.60**	**59**	**<4.0**	**143,000**	**2.0**	**510**
8/1/07 20:16	**17**	**16**	**3,400**	**24**	**e.60**	**69**	**5.3**	**142,100**	**2.3**	**670**
8/1/07 21:15	16	16	3,400	22	<1.2	65	2.7	33,600	1.8	680
8/1/07 22:15	14	12	3,300	22	<1.2	58	7.6	156,000	2.1	520
8/1/07 23:15	15	5.7	3,600	18	.50	50	1.7	163,200	1.7	170
8/2/07 0:15	14	13	3,300	19	<1.2	54	e2.2	152,000	1.6	520
8/2/07 1:15	15	13	3,500	22	<1.2	60	<4.0	158,000	2.1	520
8/2/07 2:15	15	15	3,400	21	<1.2	64	<4.0	168,000	2.0	660
8/2/07 3:15	13	14	3,200	22	<1.2	60	4.5	156,000	2.4	640
8/2/07 4:15	14	15	3,400	23	<1.2	66	<4.0	166,000	2.2	630
8/2/07 5:15	14	14	3,500	21	e.60	63	<4.0	166,000	2.3	550
8/2/07 6:15	13	15	3,600	23	e.60	63	<4.0	164,000	2.2	620
8/2/07 7:15	**13**	**17**	**3,500**	**25**	**e.60**	**68**	**<4.0**	**153,000**	**2.7**	**670**
8/2/07 7:16	**13**	**16**	**3,300**	**22**	**e.60**	**66**	**<4.0**	**149,000**	**2.5**	**670**
8/2/07 8:15	13	7.8	3,500	20	.50	50	.84	143,000	2.4	660
8/2/07 9:15	15	6.1	3,500	19	.54	50	4.7	120,000	3.1	150
8/2/07 10:15	10	15	3,300	19	e.60	55	4.1	120,000	2.7	630

Appendix 2. Water-quality data from Grape Creek at streamgage SW1, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. —Continued

[M/D/Y, month/day/year; HH:MM, hour:minute; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; e, estimated concentration; –, no data; duplicate samples in bold]

Date and time of sample collection (M/D/Y HH:MM)	Barium (µg/L)	Beryllium (µg/L)	Boron (µg/L)	Cadmium (µg/L)	Chromium (µg/L)	Cobalt (µg/L)	Copper (µg/L)	Iron (µg/L)	Lead (µg/L)	Lithium (µg/L)
8/2/07 11:15	15	7.6	3,400	22	0.58	52	1.4	113,000	3.4	640
8/2/07 12:15	15	7.0	3,400	21	.52	48	1.3	104,000	3.2	190
8/2/07 13:15	19	5.7	3,600	20	.50	47	1.4	93,400	3.3	140
8/2/07 14:15	17	6.2	3,600	19	.50	48	1.9	87,600	2.9	160
8/2/07 15:15	18	6.1	3,400	20	.50	49	1.3	102,000	3.2	150
8/2/07 16:15	18	10	3,600	21	.56	56	1.6	96,800	3.3	680
8/2/07 17:15	14	14	3,300	20	e.60	55	e3.0	90,000	2.7	570
8/2/07 18:15	17	10	3,400	23	e.70	51	e2.5	102,000	3.0	300
8/2/07 19:15	15	13	3,500	19	<1.2	52	7.7	116,000	2.7	530
8/2/07 20:15	16	8.2	3,400	20	e.60	45	<4.0	116,000	2.6	260
8/2/07 21:15	14	14	3,300	19	e.60	57	e2.2	127,000	2.0	640
8/2/07 22:15	14	15	3,500	21	e.60	57	11	150,000	2.5	600
8/2/07 23:15	20	6.4	3,300	20	e.60	48	<4.0	127,000	2.6	610
8/3/07 0:15	13	15	3,200	22	.70	59	e2.7	136,000	2.1	560
8/3/07 1:15	13	9.2	3,600	20	<1.2	50	<4.0	147,000	2.0	290
8/3/07 2:15	**10**	**14**	**3,500**	**18**	**e.60**	**55**	**<4.0**	**146,000**	**2.0**	**610**
8/3/07 2:16	**13**	**15**	**3,400**	**22**	**e.70**	**58**	**7.1**	**159,000**	**2.4**	**580**
8/3/07 3:15	14	8.9	3,500	20	e.60	51	<4.0	156,000	2.2	280
8/3/07 4:15	13	14	3,200	21	e.80	61	e2.4	152,000	2.1	520
8/3/07 5:15	14	19	3,400	24	e.80	70	e2.1	164,000	2.5	760
8/3/07 6:15	12	16	3,200	21	e.70	60	<4.0	159,000	2.0	620
8/3/07 7:15	**10**	**12**	**3,600**	**19**	**<1.2**	**54**	**e2.3**	**159,000**	**2.0**	**530**
8/3/07 7:16	**12**	**10**	**3,400**	**20**	**e.60**	**52**	**<4.0**	**160,000**	**2.4**	**300**
8/3/07 8:15	13	17	3,200	23	e.70	63	<4.0	134,000	3.0	620
8/3/07 9:15	11	13	3,400	19	<1.2	53	e2.4	118,000	2.6	550
8/3/07 10:15	14	8.5	3,500	20	.62	61	1.6	107,000	3.7	660
8/3/07 11:15	12	14	3,500	20	<1.2	54	2.2	113,000	3.2	580

Appendix 2. Water-quality data from Grape Creek at streamgage SW1, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. —Continued

[M/D/Y, month/day/year; HH:MM, hour:minute; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; e, estimated concentration; –, no data; duplicate samples in bold]

Date and time of sample collection (M/D/Y HH:MM)	Manganese (µg/L)	Molybdenum (µg/L)	Nickel (µg/L)	Selenium (µg/L)	Silver (µg/L)	Strontium (µg/L)	Thallium (µg/L)	Uranium (µg/L)	Vanadium (µg/L)	Zinc (µg/L)
8/1/07 11:15	**3,700**	**<1.2**	**250**	**0.80**	**<1.0**	**540**	**0.16**	**0.16**	**3.5**	**61,000**
8/1/07 11:16	**3,800**	**<1.2**	**320**	**.80**	**<1.0**	**550**	**.16**	**.16**	**3.7**	**61,400**
8/1/07 12:15	3,600	<.2	380	.74	<.2	550	.16	.18	3.8	61,000
8/1/07 13:15	3,800	<1.2	260	e.70	<1.0	550	<.40	e.20	2.5	52,500
8/1/07 14:15	3,900	<.1	360	.64	<.1	500	.15	.20	2.1	61,600
8/1/07 15:15	3,900	<1.2	280	e.50	<1.0	560	e.20	e.20	3.3	58,200
8/1/07 16:15	3,600	<1.2	260	.80	<1.0	540	e.20	e.20	2.8	58,300
8/1/07 17:15	4,400	<1.2	320	1.0	<1.0	840	e.20	e.20	3.9	60,700
8/1/07 18:15	4,300	<1.2	310	1.1	<1.0	820	e.20	e.20	3.5	58,200
8/1/07 19:15	4,300	<1.2	320	1.0	<1.0	800	<.40	e.20	4.1	61,700
8/1/07 20:15	**3,800**	**<1.2**	**280**	**e.70**	**<1.0**	**690**	**e.20**	**<.40**	**4.1**	**60,600**
8/1/07 20:16	**4,400**	**<1.2**	**330**	**1.1**	**<1.0**	**810**	**e.20**	**e.20**	**4.6**	**61,500**
8/1/07 21:15	4,100	<1.2	300	1.1	<1.0	770	<.40	<.40	<.40	60,600
8/1/07 22:15	3,700	<1.2	280	.80	<1.0	680	.2	<.40	3.8	59,400
8/1/07 23:15	3,000	<1.2	320	.50	<1.0	440	.14	.10	4.0	63,200
8/2/07 0:15	3,400	<1.2	260	.80	<1.0	660	<.40	<.40	3.6	55,900
8/2/07 1:15	3,800	<1.2	290	.80	<1.0	700	e.20	<.40	4.2	60,600
8/2/07 2:15	4,100	<1.2	300	.90	<1.0	770	e.20	<.40	4.0	59,200
8/2/07 3:15	3,700	<1.2	280	.90	<1.0	720	e.20	<.40	4.3	58,000
8/2/07 4:15	4,100	<1.2	310	.90	<1.0	800	e.20	<.40	4.9	61,100
8/2/07 5:15	4,100	<1.2	300	.80	<1.0	620	e.20	<.40	5.1	61,600
8/2/07 6:15	3,900	<1.2	300	1.00	<1.0	750	e.20	<.40	4.8	64,300
8/2/07 7:15	**4,200**	**<1.2**	**320**	**1.0**	**<1.0**	**790**	**e.20**	**<.40**	**5.1**	**62,100**
8/2/07 7:16	**4,100**	**<1.2**	**310**	**1.1**	**<1.0**	**750**	**e.20**	**<.40**	**4.9**	**60,400**
8/2/07 8:15	3,000	<1.2	370	.60	<1.0	450	.14	.10	3.8	61,500
8/2/07 9:15	2,900	<.2	380	.56	<.2	430	.14	.10	3.7	61,200
8/2/07 10:15	3,500	<1.2	270	e.60	<1.0	500	<.40	<.40	4.4	60,800

Appendix 2. Water-quality data from Grape Creek at streamgage SW1, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007. —Continued

[M/D/Y, month/day/year; HH:MM, hour:minute; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; e, estimated concentration; –, no data; duplicate samples in bold]

Date and time of sample collection (M/D/Y HH:MM)	Manganese (µg/L)	Molybdenum (µg/L)	Nickel (µg/L)	Selenium (µg/L)	Silver (µg/L)	Strontium (µg/L)	Thallium (µg/L)	Uranium (µg/L)	Vanadium (µg/L)	Zinc (µg/L)
8/2/07 11:15	3,100	<0.2	390	0.58	<0.2	450	0.16	0.12	3.6	61,000
8/2/07 12:15	2,900	<.2	290	.56	<.2	440	.14	.14	3.2	59,100
8/2/07 13:15	2,900	<.2	400	.50	<.2	440	.14	.18	2.6	60,000
8/2/07 14:15	3,000	<.2	390	.56	<.2	510	.14	.18	2.6	60,100
8/2/07 15:15	2,800	<.2	350	.52	<.2	450	.16	.18	2.8	57,600
8/2/07 16:15	3,700	<.2	320	.66	<.2	460	.16	.20	3.1	62,600
8/2/07 17:15	3,500	<1.2	270	e.50	<1.0	540	<.40	<.40	3.4	54,300
8/2/07 18:15	3,600	<1.2	260	e.50	<1.0	490	e.20	e.20	3.5	59,300
8/2/07 19:15	3,300	<1.2	250	e.50	<1.0	550	<.40	<.40	3.3	60,600
8/2/07 20:15	3,100	<1.2	230	e.40	<1.0	450	<.40	<.40	3.2	60,800
8/2/07 21:15	3,700	<1.2	280	e.70	<1.0	530	<.40	<.40	4.0	56,200
8/2/07 22:15	3,800	<1.2	280	e.70	<1.0	560	e.20	<.40	3.9	62,000
8/2/07 23:15	3,600	<1.2	280	e.50	<1.0	430	<.40	<.40	3.6	57,800
8/3/07 0:15	3,900	<1.2	290	.80	<1.0	550	e.20	<.40	4.1	57,100
8/3/07 1:15	3,300	<1.2	260	e.50	<1.0	450	<.40	<.40	4.3	65,200
8/3/07 2:15	**3,400**	**<1.2**	**270**	**e.60**	**<1.0**	**510**	**<.40**	**<.40**	**4.2**	**59,600**
8/3/07 2:16	**4,000**	**<1.2**	**290**	**1.0**	**<1.0**	**540**	**e.20**	**<.40**	**5.0**	**63,200**
8/3/07 3:15	3,400	<1.2	260	e.50	<1.0	470	e.20	<.40	4.2	63,600
8/3/07 4:15	4,000	<1.2	300	e.60	<1.0	540	e.20	<.40	4.8	58,000
8/3/07 5:15	4,600	<1.2	330	1.0	<1.0	660	e.20	<.40	5.8	61,000
8/3/07 6:15	3,900	<1.2	290	.90	<1.0	560	<.40	<.40	5.2	57,200
8/3/07 7:15	**3,300**	**<1.2**	**260**	**e.60**	**<1.0**	**540**	**<.40**	**<.40**	**4.1**	**62,100**
8/3/07 7:16	**3,500**	**<1.2**	**270**	**e.50**	**<1.0**	**450**	**e.20**	**<.40**	**4.7**	**62,000**
8/3/07 8:15	4,100	<1.2	310	.90	<1.0	590	e.20	<.40	4.7	59,200
8/3/07 9:15	3,400	<1.2	260	e.60	<1.0	590	<.40	<.40	3.3	59,000
8/3/07 10:15	3,600	<.2	270	.54	<.2	580	e.20	<.40	3.8	63,200
8/3/07 11:15	3,400	<1.2	260	e.60	<1.0	620	<.40	<.40	3.4	62,200

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[1] Concentrations of sulfate based on calculation of electroneutrality of sample solution.

Appendix 3. Nitrogen compound data from Grape Creek at streamgage SW1, Hegeler Zinc Superfund site, near Hegeler, Illinois, August 1–3, 2007.

[M/D/Y, month/day/year; HH:MM, hour:minute; mg/L, milligrams per liter; e, estimated concentration; <, less than; duplicate samples in bold]

Date and time of sample collection (M/D/Y HH:MM)	Nitrite and nitrate, as nitrogen (mg/L)	Nitrite, as nitrogen (mg/L)
8/1/07 11:15	**<0.06**	**0.01**
8/1/07 11:16	**<.06**	**e.006**
8/1/07 12:15	<.06	e.006
8/1/07 13:15	<.06	.004
8/1/07 14:15	<.06	.004
8/1/07 15:15	<.06	.004
8/1/07 16:15	<.06	.005
8/1/07 17:15	<.06	.006
8/1/07 18:15	<.06	.003
8/1/07 19:15	<.06	.002
8/1/07 20:15	**<.06**	**<.002**
8/1/07 20:16	**<.06**	**e.002**
8/1/07 21:15	<.06	<.002
8/1/07 22:15	<.06	<.002
8/1/07 23:15	<.06	<.002
8/2/07 0:15	<.06	<.002
8/2/07 1:15	<.06	<.002
8/2/07 2:15	<.06	<.002
8/2/07 3:15	<.06	<.002
8/2/07 4:15	<.06	.005
8/2/07 5:15	<.06	<.002
8/2/07 6:15	<.06	<.002
8/2/07 7:15	**<.06**	**e.001**
8/2/07 7:16	**<.06**	**<.002**
8/2/07 8:15	<.06	<.002
8/2/07 9:15	<.06	<.002
8/2/07 10:15	<.06	.002
8/2/07 11:15	<0.06	0.005
8/2/07 12:15	<.06	.005
8/2/07 13:15	<.06	.004
8/2/07 14:15	<.06	.004
8/2/07 15:15	<.06	.004
8/2/07 16:15	<.06	.005
8/2/07 17:15	<.06	.003
8/2/07 18:15	<.06	.002
8/2/07 19:15	<.06	.003
8/2/07 20:15	<.06	.002
8/2/07 21:15	<.06	<.002
8/2/07 22:15	<.06	<.002
8/2/07 23:15	<.06	<.002
8/3/07 0:15	<.06	<.002
8/3/07 1:15	<.06	.006
8/3/07 2:15	**<.06**	**<.002**
8/3/07 2:16	**<.06**	**<.002**
8/3/07 3:15	<.06	<.002
8/3/07 4:15	<.06	<.002
8/3/07 5:15	<.06	<.002
8/3/07 6:15	<.06	<.002
8/3/07 7:15	**<.06**	**<.002**
8/3/07 7:16	**<.06**	**<.002**
8/3/07 8:15	<.06	<.002
8/3/07 9:15	<.06	.003
8/3/07 10:15	<.06	.002
8/3/07 11:15	<.06	.004

Appendix 4. Composition of hypothetical minerals used in geochemical modeling of water samples collected at the Hegeler Zinc Superfund site, near Hegeler, Illinois.

Mineral	Composition	Sample environment
Albite	$NaAlSi_3O_8$	groundwater
Alunite	$KAl_3(SO_4)_2(OH)_6$	Grape Creek, groundwater
Anorthite	$CaAl_2Si_2O_8$	groundwater
Barite	$BaSO_4$	Grape Creek, groundwater
Chalcedony	SiO_2	groundwater
Clinochlore-14A	$Mg_5Al_2Si_3O_{10}(OH)_8$	groundwater
Clinochlore-7A	$Mg_5Al_2Si_3O_{10}(OH)_8$	groundwater
Cuprous Ferrite	$CuFeO_2$	Grape Creek, groundwater
Diopside	$CaMgSi_2O_6$	groundwater
Fayalite	Fe_2SiO_4	groundwater
Potassium feldspar	$KAlSi_3O_8$	groundwater
Ferrihydrite (amorphous)	$Fe(OH)_3$	Grape Creek, groundwater
$Fe(OH)_2$	$Fe(OH)_2$	Grape Creek
Forsterite	Mg_2SiO_4	groundwater
Goethite	FeOOH	Grape Creek, groundwater
Gypsum	$CaSO_4 \bullet 2H_2O$	Grape Creek, groundwater
Hematite	Fe_2O_3	Grape Creek, groundwater
Hercynite	$FeAl_2O_4$	groundwater
Jadeite	$NaAl(SiO_3)_2$	groundwater
Jarosite (solid solution)	$(K_{0.77}Na_{0.03}H_{0.2})Fe_3(SO_4)_2(OH)_6$	Grape Creek, groundwater
Jurbanite	$AlOHSO_4$	Grape Creek, groundwater
Magnetite	Fe_3O_4	groundwater
Potassium mica	$KAl_3Si_3O_{10}(OH)_2$	groundwater
Ca-Al Pyroxene	$CaAl_2SiO_6$	groundwater
Schwertmannite	$Fe_8O_8(OH)_{4.5}(SO_4)_{1.75}$	Grape Creek, groundwater
Silica gel	SiO_2	Grape Creek
SiO_2 (amorphous)	SiO_2	Grape Creek, groundwater
Sphalerite	ZnS	groundwater
Spinel	Al_2MgO_4	groundwater
ZnS (amorphous)	ZnS	groundwater

USGS

Kay and others—**Diel Sampling of Groundwater and Surface Water at a Former Zinc Smelter Site, Hegeler, Illinois, August 1–3, 2007**—Scientific Investigations Report 2009–5210