

University of Wisconsin-Extension
GEOLOGICAL AND NATURAL HISTORY SURVEY
3817 Mineral Point Road
Madison, Wisconsin 53705

M.E. Ostrom, State Geologist and Director

INVESTIGATION OF THE EFFECTS OF RECENT MINE CLOSINGS ON
GROUND-WATER QUALITY AND QUANTITY IN THE SHULLSBURG AREA

by

T.J. Evans, M.J. Cieslik, R.G. Hennings

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Investigation of the Effects of Recent Mine Closings
on Ground-Water Quality and Quantity
in the Shullsburg Area

Principal Report Submitted to Lafayette County
Board of Supervisors Pursuant to Contract for Services
with Geological and Natural History Survey
University of Wisconsin-Extension

Thomas J. Evans
Marten J. Cieslik
Ronald G. Hennings

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PREFACE AND ACKNOWLEDGMENTS

This report is submitted in partial fulfillment of a Contract for Services between the Lafayette County Board of Supervisors and the Geological and Natural History Survey, University of Wisconsin-Extension. Under the terms of the Contract for Services, this report is the Principal Report, summarizing the investigation by the Survey as of September 1, 1982.

The authors wish to acknowledge the invaluable assistance of the staff of the Wisconsin Department of Natural Resources. Specifically, thanks are expressed to Kevin Kessler, Charles Goethel, Roger Gerhardt, Gordon Reinke, Patrick McCutcheon, and Larry Lynch. In addition, the authors express their thanks to Barbara J. McKellar for her help in collecting and summarizing information on previous instances of sulfate-impacted waters associated with zinc-lead mining.

INTRODUCTION

Summary of Ground Water Problem in the Shullsburg Area

The Wisconsin Department of Natural Resources (DNR) sampled several private water-supply wells in the Shullsburg area (fig. 1; pl. 1) in the late summer and early fall of 1980. This sampling was done in response to citizen complaints about degraded water quality. Public notice of this problem was first raised in July, 1980 at a meeting called by State Representative Joseph Tregoning to discuss public concerns with the economic impact of the closing of zinc-lead mines near Shullsburg. A second public meeting was arranged in August, 1980 to deal specifically with concerns for water quality raised at the July meeting. Sampling of additional private wells by the Department of Natural Resources and a series of meetings followed and the findings from these sampling results and meetings are summarized in the Emergency Grant Application submitted by the Lafayette County Board of Supervisors to the (Mining) Investment and Local Impact Fund Board on November 24, 1980 (Dennis, 1980).

Private water-supply wells sampled by the DNR in response to citizen complaints showed that the quality of water in most of the wells sampled was poor. Typically, the water quality was characterized by high concentrations of sulfate (SO_4), as well as high levels of calcium (Ca), magnesium (Mg), total alkalinity, total hardness, manganese (Mn), total residue (dissolved solids), and iron (Fe).

Concentrations of arsenic (As) and lead (Pb) were observed in the course of DNR sampling and, later, in sampling pursuant to the Contract for Services between the Geological and Natural History Survey and Lafayette County. Three private wells had levels of arsenic or lead that exceeded the National Interim Primary Drinking Water Regulations (U.S. Environmental Protection Agency, 1975). In none of the three wells did elevated arsenic or lead concentrations appear in subsequent sampling and analysis. Therefore, evaluation of water quality in the Shullsburg area has focused on (1) elevated sulfate concentrations, (2) related elevated water-quality parameters, such as total dissolved solids, iron, manganese, and zinc--which commonly exceeded National Secondary Drinking Water Regulations (U.S. Environmental Protection Agency, 1979), and (3) other water-quality parameters, such as calcium and magnesium.

Proposal of a Relationship of Mining to the Water Problem

Public notice of the poor water quality present in private water-supply wells arose from the summer 1980 meetings noted previously. Citizens complaining of poor water quality indicated a belief that, in some way, their deteriorating water quality was related to the mining activity (specifically, the closing of Shullsburg and Bear Hole Mines). Upon water sampling and analysis, a clear spatial relationship between high-sulfate water, proximity

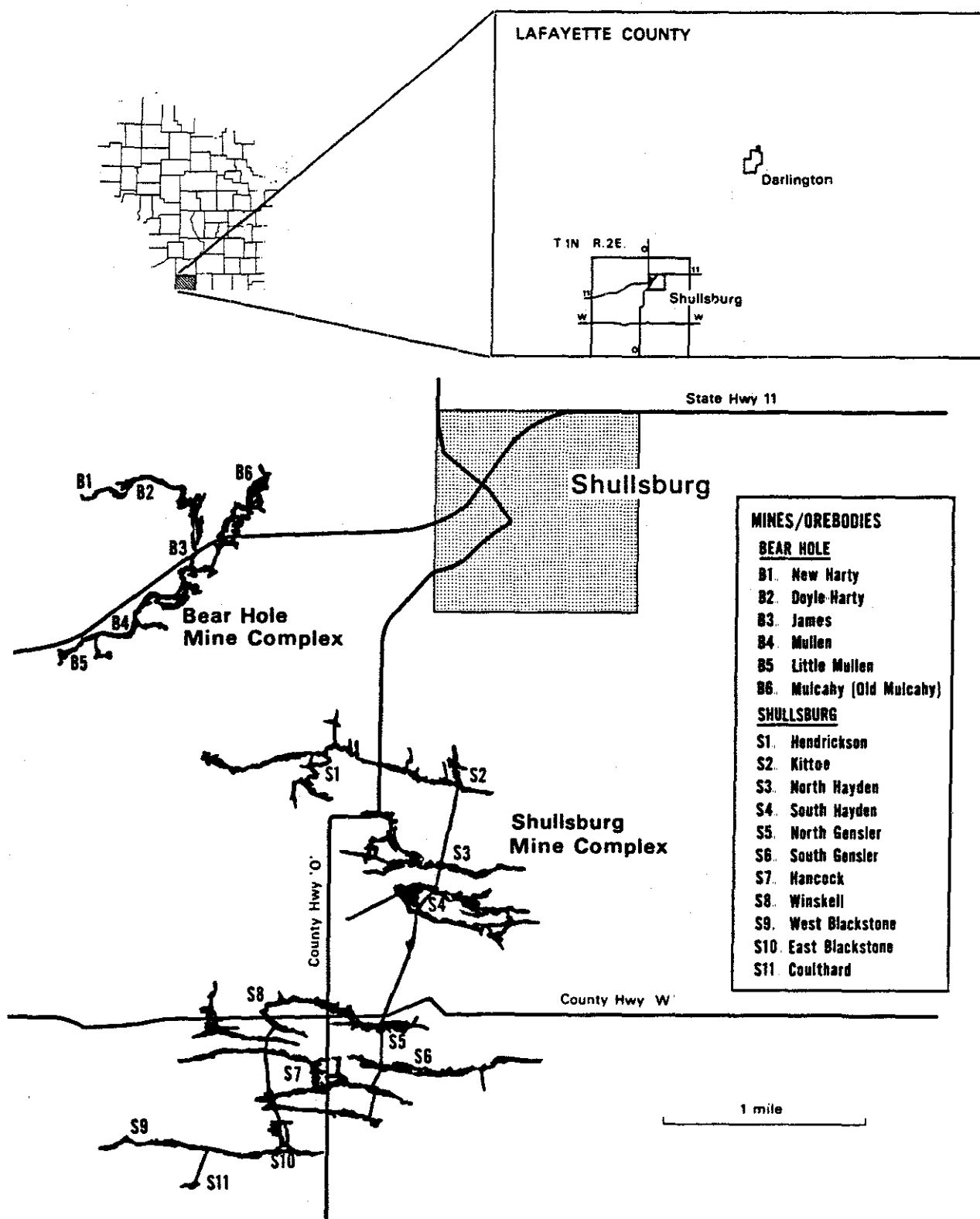


Figure 1. Map of the Shullsburg Area, Lafayette County, Wisconsin showing location of the Shullsburg and Bear Hole Mine complexes. Each complex represents a group of ore bodies or separate mines that were interconnected by underground mine drifts (tunnels).

to mined areas, and citizen complaints was observed (pl. 1). In all cases where a citizen complaint was received and high-sulfate waters were detected, the private water-supply well was near a mined area.

Further, citizen complaints about water quality arose within about one year following the closing of the Shullsburg Mine (September 29, 1979). One citizen indicated a longer history of poor quality water (going back to 1978), despite first coming forward with their complaint in the summer of 1980. This private water-supply well was located near Bear Hole Mine, which had closed in August 1978.

The observed spatial and temporal relationship between ground-water quality deterioration in the Shullsburg area and the Shullsburg and Bear Hole Mines strongly indicated that citizen perceptions of a relationship between their water quality and the mine closings were plausible. The evaluation of that postulated relationship--the degree to which available geologic, hydrologic, and mining activity data supported or did not support the relationship--became the focus of an investigation proposed by Lafayette County in its Emergency Grant Application (Dennis, 1980).

Geologic and Hydrogeologic Setting of the Area

The following description of the geology of the Shullsburg area is adapted from Mullens (1964). For more detailed information, the reader is directed to Mullens (1964) and Heyl and others (1959).

Surficial Geology

Three major bedrock units crop out in the Shullsburg area: Maquoketa Shale, Galena Dolomite, and Decorah Formation (pl. 2).

The Maquoketa Shale of Late Ordovician age ranges from a feather edge to nearly 200 feet thick in the southeast-quarter of T. 1 N., R. 2 E. The unit is a dolomitic to clayey siltstone. The Galena Dolomite of Middle Ordovician age is over 200 feet thick in the Shullsburg area and is characterized by an upper noncherty dolomite unit and a lower cherty dolomite unit of approximately equal thickness. The Decorah Formation of Middle Ordovician age is a thin (25 to 40 feet) unit comprised of limestone, dolomite, and shale. The Decorah Formation is divided, from top to bottom, into 3 members: Ion, Guttenberg, and Spechts Ferry. In addition to these units, 10 to 20 feet of Lower Silurian-age Edgewood Dolomite occurs at topographic highs on top of the Maquoketa Shale. Unconsolidated alluvium of Quaternary age occurs along most streams in the area (pl. 2).

Subsurface Geology

In addition to the Decorah Formation and Galena Dolomite, subsurface geologic units in the Shullsburg area include the Middle Ordovician age units

known as the Platteville Formation and the St. Peter Sandstone (fig. 2; pl. 3). The Platteville Formation is 55 to 75 feet thick and includes predominantly dolomite and limestone. The Platteville includes 3 members, from top to bottom, named Quimbys Mill, McGregor and Pecatonica. Beneath the Platteville lies the St. Peter Sandstone comprised of very fine to coarse, well-rounded sand grains. The uppermost St. Peter is a shaley unit ranging from 0 to 3 feet thick, known as the Glenwood Shale. The thickness of the St. Peter is highly variable ranging from 340 feet in the City of Shullsburg to about 50 feet at other places in the Shullsburg area.

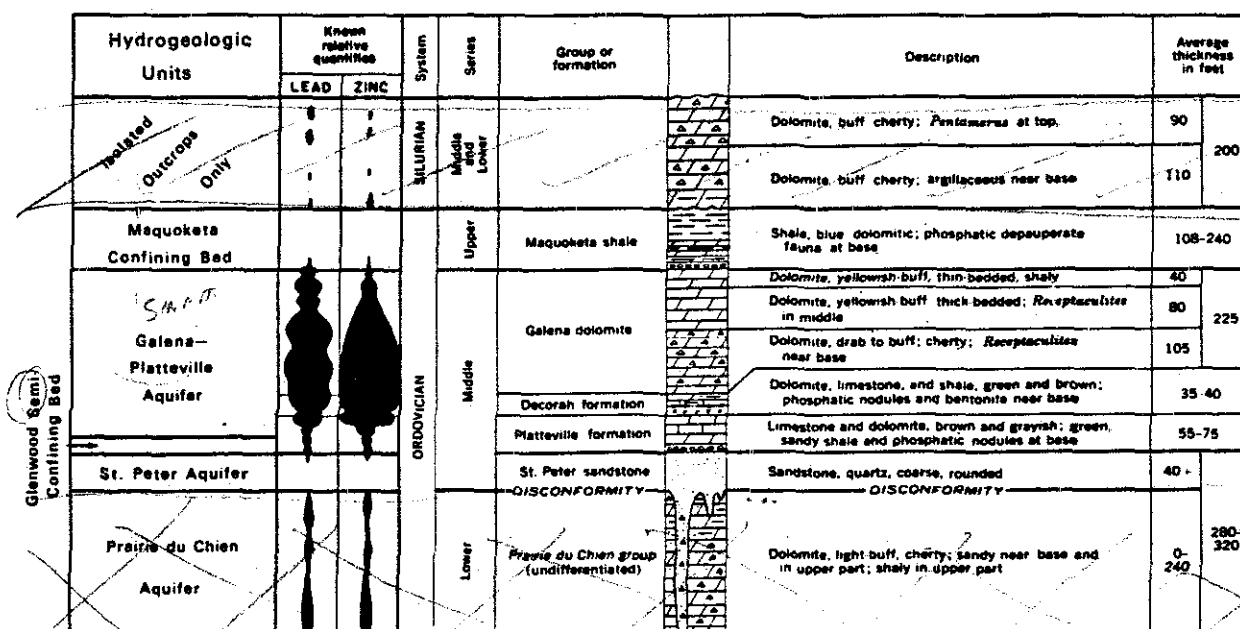


Figure 2. Generalized stratigraphic section showing relative quantitative stratigraphic distribution of lead and zinc (from Heyl and others, 1959, and Mullens, 1964) with addition of hydrogeologic units for this report.

Hydrogeologic Units

From a hydrogeologic perspective, there are four principal units governing the movement of ground water in the Shullsburg area (fig. 2). The Galena, Decorah, and Platteville rock units together comprise a single hydrogeologic unit known as the Galena-Platteville aquifer. According to Hindall and Skinner (1973), water yields from this fractured dolomite and limestone aquifer are small to moderate and water quality is considered "good". The water tends to be very "hard" and is locally high in iron. The Galena-Platteville aquifer is an unconfined (water table) aquifer in part of the Shullsburg area and is confined in the other part of the area. This reflects the presence of the Maquoketa confining bed in the southeastern part of the area, which thus makes the Galena-Platteville aquifer in that area a confined aquifer.

The St. Peter Sandstone aquifer is a second hydrogeologic unit that readily yields water to a well. Water yields from this semi-confined aquifer are reportedly very good in the immediate area. Water quality tends to be good and is generally lower in dissolved solids than the overlying Galena-Platteville aquifer. Analyses of St. Peter water sampled in the course of this investigation show that St. Peter water is distinctly different from Galena-Platteville water in the wells sampled.

The Galena-Platteville and St. Peter Sandstone aquifers are separated by a thin (0 to 3 feet thick) unit known as the Glenwood Formation. The Glenwood is hydrogeologically known as a semi-confining bed in that it has a low capability to transmit water relative to the two aquifers that it separates. However, the Glenwood is not everywhere present, is locally fractured, and even where present and unfractured will still transmit some water from one aquifer to the other. Under normal ground-water conditions, there is some component of net downward movement of water from the Galena-Platteville aquifer into the St. Peter Sandstone aquifer.

Overlying much of the southeastern part of the Shullsburg area is the Maquoketa Shale. The Maquoketa is a confining bed, that is, it has a very low capability to transmit water. The confining character of the Maquoketa means that domestic wells in the area are not capable of producing water from the Maquoketa and that recharge of surface water into the Galena-Platteville aquifer is greatly retarded wherever the Maquoketa is present above the Galena-Platteville.

General Structure

The geologic units in the Shullsburg area dip generally southward at 18 feet per mile. In addition, several broad, gentle folds are present trending generally from southwest to northeast. The folds typically extend from 1 mile to as much as 5 miles (or more in some instances) along strike. These folds have about 20 feet of structural relief. Faults are not significant in a regional sense in the Shullsburg area. A fault having 15 to 20 feet of vertical displacement occurs one mile northwest of the Bear Hole Mine area. Joints occur throughout the Shullsburg area. Vertical joints dominate and trend roughly north-south and east-west in the southern part of the area to northeast-southwest and west-northwest to east-southeast in the northern part of the area.

The type of stresses that can be called upon to produce the regional structure in the area cannot be definitely identified. Lateral compression and vertical adjustments in "basement" rocks are two postulated mechanisms of roughly equal plausibility.

Local Structure and Mineral Deposits

Mineral concentrations in the Shullsburg area are related to local structural conditions. Three types of mineral deposits occur in the area: (1) gash vein deposits associated with vertical joints, (2) deposits associated with inclined fractures (pitches) and bedding-plane fractures (flats), and (3) deposits not associated with obvious structural control. (These latter deposits are mainly lead-rich but are not important economically in the area; therefore, deposits not associated with obvious structural control are not discussed further.)

Gash vein deposits occur in the Galena Dolomite (dominantly galena--lead sulfide--mineralization above the water table) and in the Quimbys Mill and McGregor members of the Platteville Formation (dominantly sphalerite--zinc sulfide--mineralization below the water table). Production from gash veins in the Galena Dolomite is important from an historical perspective, but has not been economically significant since the late nineteenth century. Sphalerite (with galena, pyrite, marcasite, and calcite) mineralization occurs in gash veins present in the Platteville Formation. Such deposits were important in parts of the Shullsburg Mine and to a lesser extent in part of the Bear Hole Mine. The bulk of the mineralization occurred in the Quimbys Mill (glass rock) unit principally along west-to-east trending joints.

Pitch and flat mineral deposits are typically developed in the Decorah Formation, as well as the upper part of the Platteville Formation and lower part of the Galena Dolomite. "They are associated with inclined fractures, fractures parallel to bedding, extensive altered zones...., breccia, contorted beds, and synclines or basins as expressed at certain stratigraphic zones" (Mullen, 1964, p. 503). The majority of this type of deposit extends stratigraphically upwards from the Spechts Ferry member of the Decorah Formation to as much as 30 feet above the base of the Galena Dolomite. Pitch and flat deposits include the largest ore deposits in the Shullsburg area. These deposits are dominantly sphalerite with galena, pyrite, marcasite, calcite, and, to a lesser extent, barite.

Rock alteration is common near mineral deposits in the Shullsburg area. This alteration, as reflected in thinning of rock units by as much as 36% (Heyl and others, 1959, p. 103) followed by a loss of structural integrity, and related collapse causing fractures to develop and breccia zones, provides the host environment for ore mineralization. Rock alteration is evidenced by leaching of country rock in addition to solution thinning. Silicification and dolomitization are typical alteration phenomena observed in the area in proximity to ore bodies.

Sequence of Mineralization

Mineral deposits in the area show a consistent pattern or order of crystallization. A paragenetic sequence is described by Mullen (1964, p. 488,

fig. 56). Pyrite and marcasite deposition occurs early followed by sphalerite, galena and calcite. There is some overlap in mineral deposition. This sequence of mineralization is derived from the observed zonation of gash-vein and pitch-and-flat deposits which tend to show a country rock-to-ore body "layering": marcasite and pyrite—→sphalerite—→galena—→calcite.

Besides this zoning of mineral deposition in fractures and other openings, mineralization extends outward into the country rock as a replacement phenomenon. The mineralization in this setting is disseminated in the altered country rock. Disseminated replacement mineralization occurs throughout the stratigraphic section associated with sulfide mineralization in the Shullsburg area. Such zones of alteration extend out from veins or fracture fillings in the ore bodies for distances of a few to as much as 400 feet (Mullen, 1964).

GROUND-WATER QUALITY AND QUANTITY IN THE SHULLSBURG AREA

Any investigation of ground-water quality and quantity in the Shullsburg area must recognize the influence of mining activity over the years. Several underground mines and shallow lead diggings are present (pl. 1); these probably had some effect on local ground-water conditions. Underground mines located beneath the top of the zone of saturation (water table) had to be pumped in order to be worked. Shallow lead diggings generally occurred above the water table and their only effect may be to increase local rock permeability due to the excavation of soil and shallow bedrock along gash veins (mineralized vertical joints).

Underground mines were developed to extract zinc-lead ore from mineral deposits located south and west of Shullsburg (T. 1 N., R. 2 E.). These mineral deposits are part of the extensive Upper Mississippi Valley zinc-lead district. The two mine complexes involved in this current investigation--Shullsburg Mine and Bear Hole Mine--were developed to recover ore from several distinct ore bodies (fig. 1). These ore bodies were connected by underground mine drifts. Centralized ore extraction occurred initially through vertical shafts and, later, through inclined openings to the ground surface. The mined ore was transported by truck to a mill located in sec. 22, T. 1 N., R. 2 E. at the site of the Shullsburg Mine.

The ore bodies were predominantly sphalerite, with lesser amounts of galena. Marcasite and pyrite (iron sulfides) were typically present. Ore bodies were located within the zone of saturation (below the ground-water table). Therefore, mine development necessitated the removal of large volumes of water from the mine workings via centrally located pumps. In his unpublished study of mine hydrology at the Shullsburg Mine, C.L.R. Holt, Jr. of the U.S. Geological Survey indicated that up to 20 million gallons per day (mgd) were pumped from the Shullsburg Mine in the early phases of operation. By the late 1950's, pumping rates had declined to slightly more than 2 mgd. The pumping rate varied with increased pumping necessary due to large inflows of water entering the mine workings when they encountered highly fractured (and thus, permeable) ore bodies. Holt (1958) indicated flows up to 8,000 gallons per minute (gpm) or 11.5 mgd were observed when a mine drift encountered a new ore body. Eagle-Picher Industries, Inc. (1977a, 1977b) reported pumping rates of 4.9 mgd at the Shullsburg Mine (two pumps) and 1.5 mgd at the Bear Hole Mine (one pump).

Water flowed into the mines along bedding planes, solution channels, fractures and joints, and springs in the floor. In addition, water cascaded down open exploration drill holes that the mine drifts intersected (Holt, 1958).

As a result of the movement of water into the mine and the high rates of pumping needed to manage the inflow and allow mining to proceed, a large cone of depression in the ground water was developed over the mines (pl. 3). The

cone of depression, modified from Holt (undated), is shown in Plate 4 which shows the areal extent of the ground-water drawdowns (about 12 square miles) over the Shullsburg Mine in the late 1950's. Also shown on plate 3 are the cones of depression reported by Eagle-Picher Industries, Inc. in their mine-permit applications (1977a, 1977b)¹.

The cone of depression within the Galena-Platteville aquifer is of primary interest. Near mine workings, water levels were lowered significantly due to pumping. The cone was gradually less pronounced at greater and greater distances away from the mine workings. The lowering of the water table beneath the potentiometric surface of the St. Peter Sandstone aquifer resulted in upward movement of St. Peter water through joints and fractures into the mine workings where the water appears as springs in the floor (fig. 3). Holt (undated) estimated that twenty percent of the water pumped from the mine in the late 1950's was St. Peter water and he postulated that a slight cone of depression in the St. Peter potentiometric surface was developed. The water table in the Maquoketa Shale (fig. 3) is relatively unaffected by the dewatering of the mines. The reduced potential recharge resulting from the lower-permeability Maquoketa Shale being present over much of the Shullsburg Mine area (pl. 2) is reflected in the greater areal extent of the cone of depression beneath the area covered by the Maquoketa (pl. 4; see also Holt, undated).

According to Holt (undated), the areal extent of the cone of depression stabilized over time. The drawdown cone did expand in areas where mine workings were extended to develop new ore bodies. However, when the mines closed and pumps were shut off, water flowed back into the mine workings and into the dewatered portion of the rock above the mine workings. The cone of depression would be expected to rapidly decrease in areal and vertical extent. A water-level recovery graph for the main shaft of the Shullsburg Mine illustrates the rapid recovery of the water level in the Galena-Platteville aquifer (fig. 4). Water-level measurements in the mine shaft, three open exploration drill holes northwest of the mine shaft, and a private water-supply well to the southeast in June, 1982 suggest that the cone of depression has experienced significant recovery--to the point that the depression of the water surface is only slightly expressed or nearly flat-lying. Additional water-level data is needed to monitor water-level recovery more precisely.

¹ The small areal extent of the cones of depression reported by Eagle-Picher most likely reflects a lack of data on water levels. The mines were more extensive in the mid-1970's (pl. 4) and pumping rates, as indicated by the mine permit applications, were larger when compared to the late 1950's. Therefore, it is reasonable to expect the areal extent of the cone of depression in the 1970's was at least as large as shown using actual water-level data from the late 1950's.

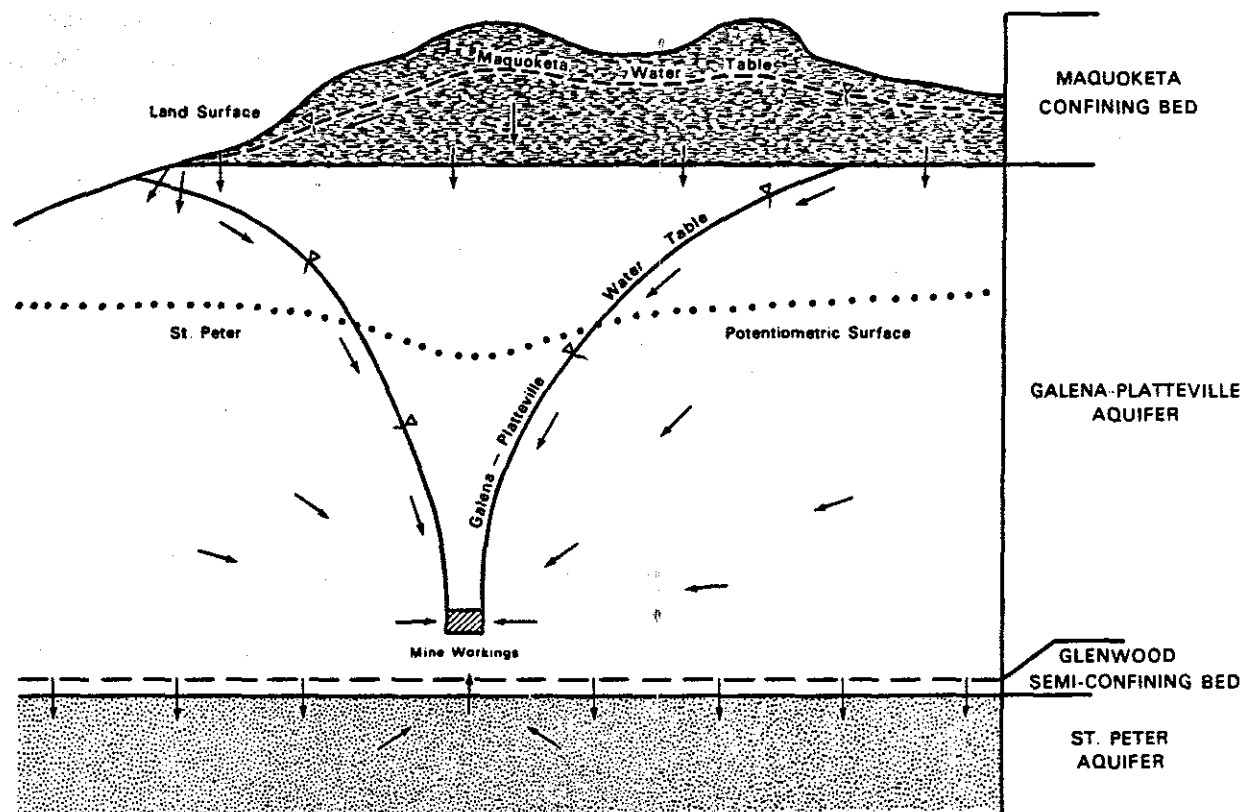


Figure 3. Idealized ground-water conditions during active mining in the Shullsburg Mine (modified from Holt, undated). Arrows show inferred directions of ground-water flow. Dashed line at top of Glenwood semi-confining bed indicates the irregular occurrence of the Glenwood in this general area.

The Bear Hole Mine closed in August 1978 and ground-water levels have now reached the level of the entry portal or incline, which is at about 865' above sea level. Upon completion of the proposed reclamation plan (Eagle-Picher Industries, Inc., 1977b), it is expected that some additional recovery of the ground-water levels in the area will occur. The Shullsburg Mine ceased mining operations and turned off water pumps on September 29, 1979. Water levels to date have reached about 915' above sea level (about 150' above the deepest portion of the mine floor) and water-level recovery is expected to slowly continue to approach the 1050' elevation (elevation of the incline entry) (Eagle-Picher Industries, Inc., 1977a). Pre-mining (circa 1947) water table elevation in the vicinity of the main shaft was about 1050' above sea level (Hindall and Skinner, 1973), so further recovery of the water table following completion of the reclamation plan, which includes filling the incline, is not expected.

Once the ground-water levels have recovered to their approximate original position at the Bear Hole and Shullsburg Mines, the pre-mining ground-water flow patterns should be reestablished. These flow patterns include flow

generally following topography (towards topographically low areas including the streams) as well as some flow vertically down from the Galena-Platteville aquifer into the semi-confined St. Peter Sandstone aquifer.

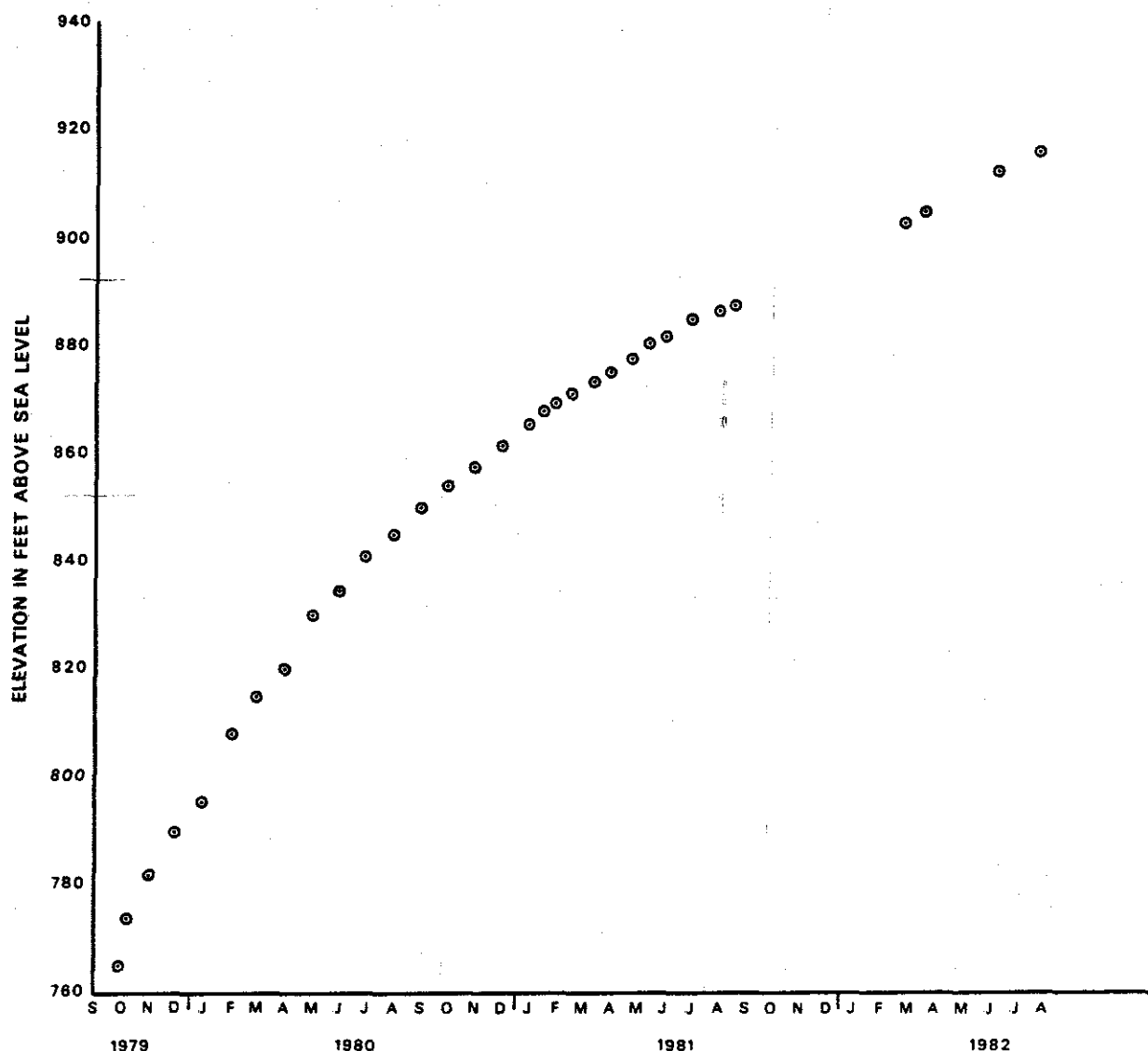


Figure 4. Graph of water-level recovery in main shaft at Shullsburg Mine complex (data courtesy of Eagle-Picher Industries, Inc. and Inspiration Mines, Inc.). Original (pre-mining) water level is about 1050 feet above sea level (data from Holt, undated).

Pre-Mining Ground-Water Conditions

Establishing pre-mining ground-water quality and quantity conditions in the Shullsburg area is difficult because lead diggings and underground zinc-lead mining occurred as long ago as the mid-1800's (Heyl and others, 1959). In the immediate vicinity of the Bear Hole Mine, mineral development necessi-

tating pumping of water began sometime between 1920 and 1924 (Heyl and others, 1959; Eagle-Picher Industries, Inc., 1977b). Shullsburg Mine development was initiated in late 1948 (Holt, undated). Water-level data from January, 1947 used by Holt in his unpublished study indicate that pre-mining water quantity was relatively unaffected by prior mine development. The reason for this relationship follows from the lack of any active major mine development in the area at that time.

Water-quality information prior to mine development in the Shullsburg area is equally sparse. Well construction reports dated prior to both the Bear Hole Mine (and predecessor mines) and Shullsburg Mine development indicate that potable water was available in domestic wells. Certainly, the existence of households, dairy farms, and other consumers in the area served by private water-supply wells prior to mining is indicative of the availability of suitable water quality. However, no actual water analyses that date back to pre-mining times are known to exist in the Shullsburg area of Lafayette County.

Ground-Water Conditions During Mining

Bear Hole Mine

History of Development.--The Bear Hole Mine is actually a complex of several small mines that are now interconnected. The history of the Bear Hole is complicated but can be summarized by quoting the 1977 mine-permit application (Eagle-Picher Industries, Inc., 1977b, p. 2):

The Bear Hole Mine...is comprised of several interconnecting smaller mines primarily the James, New Harty, Mullen, Doyle-Harty and Old Mulcahy Mines.

The James and Mullen parts of the ore body were discovered by drilling by The Vinegar Hill Mining Co. between 1920 and 1924. During the same years the New Jersey Zinc Co. discovered the Doyle-Harty ore body. The Vinegar Hill Zinc Co. opened and operated the James, Mullen and Doyle-Harty Mines from 1925 to 1936. The Gill Brothers Mining Co. re-entered and operated the James Mine from July, 1942 to July, 1946 for mining and [pillar] robbing. From March to August, 1947, Murray and Richards operated the mine. In February, 1951 Murray and Richards re-opened the James Mine and operated through 1953. About 1954 they closed the James Mine part and moved the operations to the Doyle-Harty which they worked until May, 1957.

In October, 1942 the Deuce Mining Co. re-opened the western part of the Doyle-Harty Mine. This operation was fairly

continuous until February, 1948 and was called the New Harty Mine.

The Little Mullen Mining Co. re-opened a part of the Mullen ore body near the southwest end of this ore body in May, 1944 and mined intermittently until about 1952.

The Mulcahy Mine was operated during World War I by The Oliver Iron Mining Co. It was operated again from 1941 until June, 1947 by the C.F. & H. Mining Co.

The American Zinc Co. re-opened the Bear Hole in early 1968 and operated it until June, 1970. Eagle-Picher began operations in May of 1973.

Eagle-Picher Industries, Inc. suspended operations on the Bear Hole Mine in August, 1978. Under the terms of their mining permit, the state-approved reclamation plan for Bear Hole Mine need not be initiated until February 21, 1984.

Water Quantity.--Water quantity information for the Bear Hole Mine area during active mining is generally lacking. According to Heyl and others (1959), the James Mine--one of the principal ore developments in the complex--required pumping 500 gpm or 720,000 gpd to accomplish mine dewatering. Holt (undated) reports that in 1955, during which the James Mine was active for a few months, the water level was lowered 60 feet--sufficient to dewater the mine. Nearly full water-level recovery had occurred in less than 6 months following the mine's closing in August, 1955. During the more recent operation of Bear Hole Mine, Eagle-Picher Industries, Inc. (1977b) indicated a pumping rate of 1,010 gpm or 1.5 million gpd. This removal of water created a cone of depression in the vicinity of the mine workings and which is shown on Plates 3 and 4. The areal extent of the Bear Hole Mine cone of depression is probably larger than indicated by the mining company in its 1977 mine-permit application, as suggested by the relationship between the company's estimated cone of depression and the cone of depression defined by actual well measurements for the Shullsburg Mine (Eagle-Picher Industries, Inc., 1977a; Holt, undated).

Following closure in August, 1978, the water levels have recovered to the 865-foot elevation (elevation of mouth of incline mine-portal), which is near the original water-table elevation of approximately 875' above mean sea level (Hindall and Skinner, 1973; Holt, undated; Eagle-Picher Industries, Inc., 1977b).

Water Quality.--Eagle-Picher Industries, Inc. (1977b) reported on surface-water and ground-water quality in the vicinity of Bear Hole Mine. Surface-water quality determined is a reflection of mine-water discharge quality, since during active mining the surface stream in this area flowed in response

to the discharge of mine water into the stream. The ground-water quality reported in the Bear Hole Mine permit application also reflects the mine-water discharge quality. This relationship is expected, of course, since the mine-water discharge was essentially ground water entering the mine workings through fractures, bedding planes, and open drillholes. Flow toward the mine is in response to the hydrologic gradients toward the mine created by the pumping necessary to keep the mines dewatered and in a condition suitable for mining.

Private water-supply wells near Bear Hole Mine apparently produced water of suitable quality for domestic use. Hindall and Skinner (1973) indicated that water quality in the general region was fair-to-good. Potable water supplies in both the St. Peter Sandstone (near the mines) and the Galena-Platteville aquifer (further distance away from the mines) were available.

Shullsburg Mine

History of Development.--Calumet and Hecla Consolidated Copper Co. instituted an exploration program in the area in 1947. Upon discovery of the ore bodies in sec. 22, T. 1 N., R. 2 E., a development shaft was sunk beginning in November, 1948 and was completed in 1949 (Heyl and other, 1959; Holt, undated) to a depth of 765' above mean sea level or between 330-350' below the land surface. Initial development drifts were constructed in 1949, northeastward to the South Hayden orebody and southwestward to the North Gensler ore body. Continuing development on the Gensler orebodies and the Hayden orebodies occurred throughout the 1950's. In 1954, Eagle-Picher Industries, Inc. purchased the Calumet and Hecla properties and continued zinc-lead ore production. In 1963, following a mine fire and renovation of the mill that closed operations from January through July, an inclined adit was constructed to permit diesel-powered truck haul of broken ore. This incline extended 1500 feet to the northeast from its opening west of the tailings pile. The incline replaced the skip-and-hoist method of ore removal via the main shaft.

A second group of orebodies known collectively as the Blackstone, was put into development in section 28, T. 1 N., R. 2 E. in 1949 by Vinegar Hill Zinc Company. The 283-foot shaft was completed by March, 1950. In addition to the initial development of the Blackstone ore, the nearby Hancock orebody was opened in 1952. In 1955, Vinegar Hill's operations in this area were acquired by American Zinc, Lead and Smelting Company, and continued expansion of the mine development resulted in the Coulthard orebody being opened as well as the Winskell (mined under a sublease by Eagle-Picher). Mining in the Blackstone complex stopped in September, 1957 but pumps were left on until April, 1958. In late 1959 intermittent production resumed. In 1968, The American Zinc holdings ceased operation and these properties were acquired in 1970 by Eagle-Picher Industries, Inc. Eagle-Picher focused mineral development in the Hancock and Winskell orebodies north of the Blackstone. The two complexes--Blackstone (including the Hancock and Winskell) and the Shullsburg--were connected underground.

Eagle-Picher Industries, Inc. closed the Shullsburg Mine on September 29, 1979. At the time of its closing, the Shullsburg Mine was the largest in the history of the Upper Mississippi Valley zinc-lead district. The state-approved reclamation plan is scheduled to begin in February, 1984, but initial reclamation projects on the property are already underway.

Water Quantity.--The early history of dewatering for mine development has been recounted by Holt (undated). Much of what follows is extracted from the Holt manuscript. The construction of the Shullsburg shaft and initial drift development was confronted with about 4 million gpd of water. The relatively unfractured dolomite bedrock in the immediate vicinity of the shaft kept water inflow manageable. Upon intersecting an orebody, which was present typically within highly fractured bedrock, water flows would sharply rise up to 8-11 million gpd (South Hayden orebody) and as much as 17 million gpd (North Gensler orebody). Such variations in water inflow to the mine workings was common in the Shullsburg Mine.

During development of the Blackstone ore bodies, water inflow was a persistent problem. At the time of construction of the Blackstone shaft, flow from adjacent dewatering wells had to be increased from 2 million gpd to about 6 million gpd. Water flow varied with location within the dolomite bedrock. Following completion of the shaft and initial ore body development, water inflow declined to as low as 2.5 million gpd. The cone of depression developed as a result of pumping associated with dewatering of the Blackstone ore bodies coalesced with the Shullsburg Mine cone of depression shortly following the initiation of Blackstone development.

Holt (undated) reports that the cone of depression developed by dewatering the Shullsburg Mine (including the Blackstone) stabilized with time. The 1958 areal extent of the cone of depression is about 12 square miles (pl. 4). The line of furthest extent (line of near-zero drawdown) for the cone of depression is considered reasonably accurate to the east, southeast, and south since additional orebodies developed in these directions were not extensive. However, the construction of the development drifts and mining on the Winskell and Hancock ore bodies and, particularly, the development of the Kittoe ore body probably resulted in westward and northwestward expansion of the area dewatered by the Shullsburg Mine. Documentation of this postulated areal increase in the dewatered area is not available. Holt (undated) estimated that the dewatered portion of the Galena-Platteville aquifer in the Shullsburg (and Blackstone) Mine area encompassed 33.4 billion cubic feet, and he calculated pumping volumes of about 3.4 billion cubic feet of water, resulting in a coefficient of storage for the Galena-Platteville aquifer of 0.1. Visual examination of the map of the 1958 cone of depression with respect to post-1958 mine expansion suggests that the cone of depression was at least 10% and, perhaps, 20% larger in areal extent in 1979. This suggests that upwards of 4 billion cubic feet of water (30 billion gallons) was removed from the bedrock surrounding the Shullsburg Mine, resulting in a cone of depression of about 13-15 square miles in areal extent.

Water Quality.--The work of C.L.R. Holt, Jr. and others of the U.S. Geological Survey (Holt, undated) provides most of the analytical basis for characterizing ground-water quality in the Shullsburg area during active mining. For general characterization of ground-water quality in the Pecatonica-Sugar River Basin, see Hindall and Skinner (1973).

Samples of ground water were collected in the vicinity of the Shullsburg Mine, within the mine workings, and in wells constructed very close to the mine drifts and slopes. These data are summarized in Table 1, which has been modified from Table 4 of Holt (undated). The State Laboratory of Hygiene performed the chemical analysis of the ground-water samples, with the exception of a few mine-workings samples and the five wells completed in only the Galena-Platteville aquifer (these other samples were analyzed by the U.S. Geological Survey Quality of Water Branch). The increase in sulfate and decrease in iron content in waters sampled from the wells near the mines and open to both the Galena-Platteville and St. Peter Sandstone aquifers was attributed by Holt (undated) to oxidation of insoluble sulfide minerals to soluble sulfate forms and the precipitation of oxidized iron. Similar reasoning applied to the waters sampled in the mine workings within the Galena-Platteville aquifer.

The mining-permit application for the Shullsburg Mine and Mill Unit (Eagle-Picher Industries, Inc., 1977a) relates water-quality information for the two discharge points in the Shullsburg project area (Table 2). The "effluent" described represents water pumped from the mine, part of which has been used in the mill operations, and upon mixing of both mine and mill effluent was discharged into a nearby stream pursuant to a Wisconsin Pollution Discharge Elimination System (WPDES) permit. The "ground-water" data represents water quality from water pumped from the mines without the addition of water that has been part of the mill processing operation. The Shullsburg discharge point is located in NE $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 22, T. 1 N., R. 2 E. and the Blackstone discharge point is located in NW $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 28, T. 1 N., R. 2 E.

Ground-Water Conditions After Mining

Water Quantity

Bear Hole Mine.--Following closure of the Bear Hole Mine in August, 1978, the water level in and about the mine area began to rise. No water-level data during the most recent period of mine activity at the Bear Hole Mine is available, though the approximate areal extent of the cone of depression resulting from pumping out the water entering mine workings has been noted on Plate 4. Holt (undated) indicated drawdown of up to 60 feet occurred during active mining of the James Mine (a predecessor of the Bear Hole Mine) in mid-1955. Following pump shutdown, water levels had recovered 40 feet in four months.

Table 1.--Arithmetic-average values of selected chemical constituents in ground water from wells and mine workings in the Shullsburg area (data from an unpublished manuscript by C.L.R. Holt, Jr., U.S. Geological Survey). Values shown are in parts per million (ppm) except for pH; lower figure in italics is number of analyses averaged.

Principal Aquifer	Iron (Fe)	Manganese (Mn)	Lead (Pb)	Zinc (Zn)	Calcium (Ca)	Magnesium (Mg)	Bicarbonate (HCO ₃)	Sulfate (SO ₄)	Chloride (Cl)	Dissolved Solids	Hardness as CaCO ₃	pH
Galena- Platteville	0.6 5	0.9 5	-- 0	-- 0	-- 0	-- 0	374. 5	33. 5	4.6 5	405. ^a 5	377. 5	7.4 5
Galena- Platteville and St. Peter Sandstone	0.45 13	0. 10	.003 5	.44 5	74. 3	42. 3	377. 11	75. 13	1.6 3	366. 5	377. 13	7.3 13
St. Peter Sandstone	1.48 7	0. 4	.05 7	.25 7	61. 4	35. 4	348. 4	8. 7	1.6 4	277. 7	274. 7	7.5 7
Galena- Platteville (Samples col- lected within mine workings)	0.14 12	0. 12	.02 10	.37 10	113. 10	61. 10	395. 13	203. 13	4.4 9	653. 13	553. 13	7.6 13

^a Computed from electrical specific-conductance measurements.

Table 2.--Water-quality parameters during mining as reported in the 1977 mine-permit application of Eagle-Picher Industries, Inc. for the Shullsburg Mine and Mill. Values shown are arithmetic averages of twice-monthly sampling during 1976. All values (except pH) are in milligrams per liter.

Sample	Total Solids	Suspended Solids	Lead (Pb)	Zinc (Zn)	Copper (Cu)	Alkalinity as CaCO ₃	C.O.D. ^a	Sulfates (SO ₄)	NH ₄ -N ^b	KJ-N ^c	Oil and Grease	pH	
												Minimum	Maximum
Shullsburg Effluent	1321	7.5	0.01	0.64	0.03	306	7	567	2.2	1.1	4.1	6.5	7.2
Shullsburg Ground Water	743	2.5	0.01	1.10	0.03	392	45	478	0.32	0.92	5.5	6.8	6.8
Blackstone Effluent	1044	6.5	0.01	2.24	0.03	352	2.0	406	0.10	0.11	3.6	6.6	7.1
Blackstone Ground Water	743	2.5	0.01	2.24	0.03	344	2.5	234	0.09	0.75	3.8	6.8	6.8

^a C.O.D. = chemical oxygen demand.

^b NH₄-N = a measure of the total nitrogen forms present and converted to ammonium ion.

^c KJ-N = a measure of the total nitrogen forms present and converted to ammonium sulfate under specified laboratory analytical procedures.

Within a relatively short period of time after closure in 1978, water filled the mine workings and discharged from the incline mine-portal located at an elevation of 865' above sea level. An approximate original water-table elevation of 875' (Eagle-Picher Industries, Inc., 1977; Hindall and Skinner, 1973) cannot be re-established until the lower-in-elevation mine portal is backfilled during the course of reclaiming the Bear Hole Mine. If drainage occurs through the reclaimed portal, further recovery of water levels in the Bear Hole Mine is not likely.

Shullsburg Mine.--Figure 4 shows the water-level recovery in the main shaft of the Shullsburg Mine. Following closure on September 29, 1979, water levels in and about the Shullsburg Mine complex began to rise. Initial water-level recovery was rapid, but in a few days recovery slowed and the rate of recovery has continued to decline up to the present (fig. 4). By September 1980, the water level had risen above the level of the highest mine workings at 850' (Harold Haman, personal communication). The water level in the main shaft is about 920 to 925 feet above sea level as of September, 1982.

Water-level measurements made in June, 1982 indicate that the former cone of depression in the vicinity of the Shullsburg Mine has been substantially reduced. The water level in the area is virtually flat at an elevation slightly above 900 feet above sea level. Because of this flattening, the hydraulic gradients are much reduced and water-level recovery is expected to be even slower in the future. The original water levels in the Shullsburg Mine area may never be completely reestablished. The presence of the extensive mine workings within the Galena-Platteville aquifer in effect increased the "bulk transmissivity" of the aquifer and may, therefore, not permit recovery of water levels to pre-mining conditions.

Water Quality

Introduction.--Ground-water quality in the vicinity of the Shullsburg and Bear Hole Mines has changed significantly following mine closure, and the end of pumping for the mine dewatering. Water sampling by the Wisconsin Department of Natural Resources pursuant to citizen complaints about well-water quality in the summer and fall of 1980 indicated that in some wells water quality had declined. Pursuant to a Contract for Services between Lafayette County and the Wisconsin Geological and Natural History Survey, the Survey continued sampling of wells in the area, including wells producing water of inferior quality (sulfate-impacted) and wells selected to provide information on non-sulfate-impacted ground water in the Shullsburg area (pl. 1). Also sampled were wells constructed in accordance with recommendations by the DNR, which had been incorporated into the Lafayette County Emergency Grant Application (November 24, 1980) to the (Mining) Investment and Local Impact Fund Board. Analyses of waters sampled pursuant to the DNR's investigations following citizen complaints and the Survey's water-sampling program under contract with Lafayette County are listed in Appendix A. A summary description

of the sampling methodology and analytical procedures used in the course of the Survey's program on behalf of Lafayette County is included in Appendix B.

Sulfate.--The complaints raised concerning water quality in the Shullsburg area in the summer and fall of 1980 were primarily that water consumption caused diarrhea. The effect in humans caused obvious physical discomfort. For dairy cattle drinking sulfate-impacted water, the response was also diarrhea with the cows then reportedly refusing to drink the water and milk production declined. Sampling of the waters in response to citizen complaints by the Wisconsin DNR showed clearly that the waters had elevated levels of sulfate. In combination with the magnesium in solution, the water developed a marked laxative character.

Sulfate levels ranged upwards to 3500 milligrams/liter (mg/l; in water of this character and temperature mg/l is approximately equal to parts per million, ppm). The aesthetic standard for sulfate is 250 mg/l (National Secondary Drinking Water Regulations, Federal Register, July 19, 1979, p. 42198). Though such regulations apply only to public water systems, the standards are useful guidelines for evaluating water quality in private water systems. Of all water samples collected and analyzed in the course of the Survey's investigation and the complaint investigations by the DNR, the sulfate levels averaged over 1800 mg/l in sulfate-impacted wells. A well or sampling point was considered to be a source of sulfate-impacted water if the sulfate level exceeded 700 mg/l ².

Of eleven wells sampled that were constructed in a manner permitting an inflow of water from both the Galena-Platteville and St. Peter Sandstone aquifers, ten were sulfate-impacted (see Appendix C, the Hendrickson well, for a discussion of the one exception). In addition, three other wells obtaining water only from the Galena-Platteville aquifer displayed elevated sulfate concentrations. Non-sulfate-impacted waters sampled in twenty different water-supply wells averaged well below the 250 mg/l secondary drinking-water guideline.

Metals.--Initial analyses of some private water supplies sampled by the DNR suggested that concentrations of certain metals may be significant to an understanding of the impact of recent mine closings on water quality in the Shullsburg area. Some analyses showed levels of arsenic and lead that could constitute a health concern for individuals; other analyses showed levels of zinc and iron in excess of aesthetic guidelines recommended for public water systems.

² This arbitrary level was selected to aid the Shullsburg Mining Impact Committee in evaluating requests for new well construction using monies granted by the (Mining) Investment and Local Impact Fund Board to Lafayette County. This level of sulfate was one of several criteria used to establish eligibility for financial assistance.

Arsenic above the health-related level of 50 micrograms/liter poses a health risk with long-term exposure (National Interim Primary Drinking Water Regulations, Federal Register, December 4, 1975; microgram/liter, $\mu\text{g/l}$, is approximately equal to parts per billion, ppb, for waters of these characteristics and temperature). This maximum contaminant level (MCL) of 50 $\mu\text{g/l}$ for arsenic was exceeded in two water samples.

Arsenic content in most samples was very low. Over 92% of the 112 analyses performed on water samples collected and reported in this Report indicate arsenic, if present, was below the detection limit for the analytical procedure used ($<10 \mu\text{g/l}$). Seven other analyses had detectable arsenic levels between 10 and 50 $\mu\text{g/l}$ (below the MCL for arsenic).

The two samples exceeding the 50 $\mu\text{g/l}$ MCL for arsenic cannot be readily explained. One sample showed 86 $\mu\text{g/l}$, but as this was from a newly constructed St. Peter Sandstone well, and subsequent sampling and analysis showed declining arsenic levels, it is postulated that the arsenic detected was a transitory phenomenon. Arsenic could be present as a trace element in marcasite, FeS_2 (Heyl and others, 1959), and it is possible that the drilling process itself, through its crushing and grinding action, could liberate arsenic-bearing materials in a way that permits its dissolution into the water on a limited scale. Natural sources for arsenic in ground water in the Shullsburg area are probably not abundant and are certainly not well understood.

The second sample with an elevated arsenic level (130 $\mu\text{g/l}$) was coupled with an unusually high lead concentration (4200 $\mu\text{g/l}$) and upon later sampling and analysis, the arsenic was not detected and lead concentration had dropped to 90 $\mu\text{g/l}$. The cause of this unusual arsenic level is not known but a natural source for this much arsenic seems unlikely. The co-occurrence of extremely high lead and arsenic suggests local contamination of the water supply with a lead arsenate herbicide, but attempts to verify this suggestion were not conclusive. The cause is simply not known.

Lead concentrations in waters sampled and analyzed ranged sporadically from below detection limits ($<3 \mu\text{g/l}$) to 4200 $\mu\text{g/l}$. Over half of the samples analyzed showed lead content below the detection limit and another 37% of the samples contained lead ranging in concentration from 3 to less than 50 $\mu\text{g/l}$. Of the 11 samples containing lead in excess of the 50 $\mu\text{g/l}$ MCL (National Interim Primary Drinking Water Regulations, Federal Register, December 24, 1975), all except one were from sulfate-impacted wells. The single value in non-sulfate-impacted waters that exceeded 50 $\mu\text{g/l}$ was from a private water-supply well that was sampled five times in the course of this investigation and all other samples collected from this well showed lead concentrations below the MCL for lead.

We believe a relationship between elevated lead and sulfate concentrations is suggested by the data. The mechanism for adding high levels of sulfate to ground water is consistent with the addition of lead, but a more detailed sampling program, beyond the scope of this investigation, is needed to evaluate that relationship in a more definitive manner.

Zinc is present in ground water in the Shullsburg area irrespective of the sulfate-impacting mechanism proposed in this report. No clear relationship exists between sulfate concentration in water and the zinc concentrations. The aesthetic standard for zinc is 5 mg/l (National Secondary Drinking Water Regulations, Federal Register, July 19, 1979). In the waters sampled and analyzed in this investigation, zinc ranged from below 0.01 mg/l (detection limit for analytical procedure used) to 33 mg/l (in waters collected near the bottom of the water column in the main shaft at the Shullsburg Mine). Nearly 80% of the samples contained zinc below the 5 mg/l level. Twenty-one of the 24 analyses with elevated (>5 mg/l) zinc were from waters also showing high sulfate levels.

In a manner analogous to lead, zinc may be added to the ground water in the Shullsburg area as a consequence of the same mechanism responsible for the addition of the sulfate. However, a more detailed and comprehensive water-quality investigation would be needed to adequately define that relationship.

Iron is present throughout the ground water in the Shullsburg area, irrespective of the particular aquifer or source of the water. Iron has a secondary (aesthetic) drinking-water guideline of 0.3 mg/l and iron analyses made by the DNR and the Survey ranged from below the detection limit of 0.01 mg/l for the analytical procedure used to 65 mg/l.

No clear relationship exists between iron and the sulfate-impacted waters sampled and analyzed for this investigation. Iron analyses are especially sensitive to collection and post-collection handling procedures. Preliminary examination of iron analyses suggests sampling and analytical procedures may have a marked effect on the iron concentrations observed in the Shullsburg area. A clearly definable relationship between iron content and the mechanism causing high sulfate in ground water must await subsequent investigation.

Conclusions.--Water quality has been significantly altered in the Shullsburg area following the closure of the Shullsburg and Bear Hole Mines. The most consistent alteration is the increase in sulfate concentrations. Other parameters show some change too. The calcium and magnesium concentrations, for example, are significantly increased in sulfate-impacted ground water. Metal content (particularly, lead, zinc, and iron) appears to be elevated, though such factors as abundant natural sources for these metals and concerns about sampling/analytical procedure do not allow us to assert an unequivocal relationship between the sulfate-adding mechanism and increased metals content.

Information available also strongly indicates that well construction plays a major role in whether or not a particular water-supply well will exhibit evidence of sulfate-impact. Wells that obtain water from both the Galena-Platteville and St. Peter Sandstone aquifers are much more likely to display evidence of the presence of sulfate-impacted ground water than wells obtaining water only from the St. Peter Sandstone aquifer. Wells obtaining water only from the Galena-Platteville aquifer near sulfide mineral concentrations within formerly dewatered rock strata are also likely to display evidence of sulfate-impact. See Figure 5 for a visual comparison of well construction methods and their significance for potential for sulfate-impact.

A related factor is the location of the well with respect to the cone of depression developed in the Galena-Platteville water-table aquifer (unconfined aquifer). Wells located within the cone of depression, particularly those close to the mine workings (and therefore near areas of disseminated sulfide mineralization and mineralization associated with structural features within the carbonate host rock), are coincidentally located where the water drawdown was greatest and well-construction methods were based on deepening former Galena-Platteville wells into the St. Peter Sandstone (resulting in a mixed aquifer well). Such wells are more likely to be sulfate-impacted than wells located on the periphery of the drawdown cone.

A Possible Mechanism for Adding Sulfate to Ground Water in the Shullsburg Area

Private water supplies near the Bear Hole and Shullsburg Mines displaying adverse water quality in the course of this investigation by the Survey and the complaint-investigations by the DNR are characterized by high concentrations of sulfate (SO_4). The lack of any primary, readily-soluble sulfate mineral³ in the predominately carbonate bedrock of the Shullsburg area suggests that a non-natural, man-induced source for the observed sulfate concentrations is most likely.

The most reasonable source for sulfate in the ground water is the oxidation of the ubiquitous sulfide minerals in the area. These minerals include primarily pyrite and marcasite (FeS_2), sphalerite (ZnS), and galena (PbS). The iron sulfide minerals, particularly marcasite, are more susceptible to oxidation and the formation of secondary, soluble sulfate minerals. Other possible sources of sulfate are (1) oxidation of sulfur in diesel fuel exhaust and (2) oxidation of sulfur in sulfide minerals contained in the waste rock and tailings piles in the region.

³ Barite, BaSO_4 , is a common primary sulfate mineral associated with some of the zinc, lead, and iron sulfide mineral deposits in the Shullsburg area. However, barite is not readily soluble and is, thus, not a significant source of sulfate in ground water.

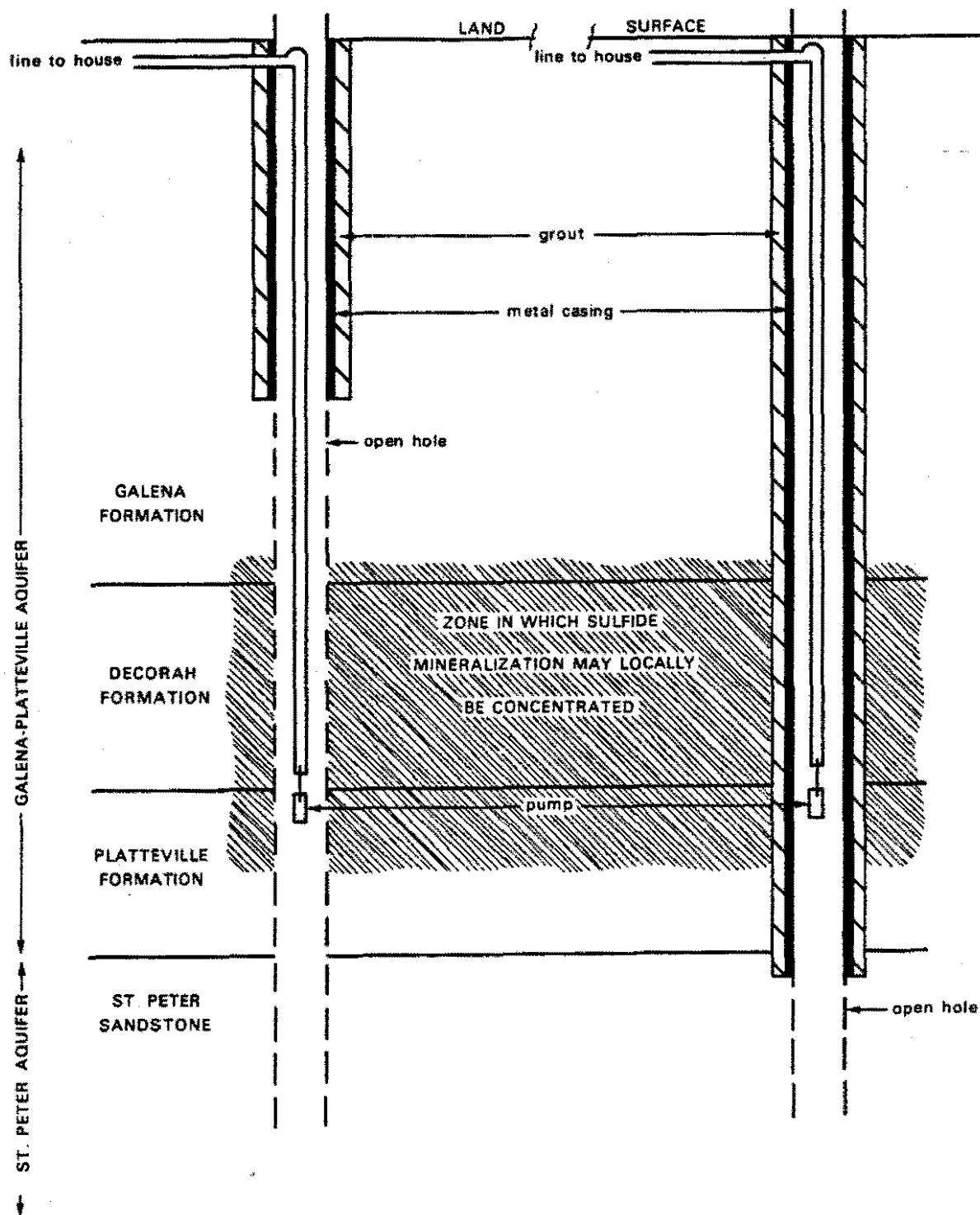


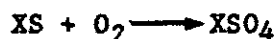
Figure 5. Well construction may help to determine if water that has been in contact with oxidized sulfide minerals (sulfates) will enter the well. The well on the left is open to water contaminated with sulfate whereas the well on the right is not; however, movement of sulfate-impacted ground water down into the St. Peter Sandstone may permit the water to enter the well on the right.

Oxidation of sulfur in diesel fuel exhaust is not considered a likely source of the sulfate in the ground water in the Shullsburg area because (1) the quantity of sulfate available to ground water from this source does not appear to be large enough to account for all the sulfate in the ground water, and (2) the spatial relationship of sulfate-impacted wells to mine workings requires that water move up hydrologic gradients to reach the wells. Sulfur content in diesel fuel is low and, though oxidation of the sulfur in the fuel residue is virtually complete (Freedman and Sharp, 1982), this minor amount of sulfate available does not appear to account for the large quantity of sulfate in the impacted ground water. Further, since hydrologic gradients in the vicinity of the mines were towards mine workings during pumping and until about mid-1982, the movement of sulfate-impacted water (from solution of sulfate in diesel-fuel-exhaust residue on the walls of mine drifts and stopes) from the mines to the nearby wells required movement of water up hydrologic gradient--an impossible circumstance.

The leaching of sulfate-impacted water from waste-rock piles and tailings basins in the area may, in fact, occur. However, consideration of this source of sulfate to account for the sulfate-impacted water fails to address (1) the temporal relationship of sulfate-impacted water supplies developing with respect to mine shutdown and (2) the spatial relationship of sulfate-impacted wells to mine workings within the central area of the ground-water cone of depression. Deteriorating water quality in private water-supply wells occurred only after mine closings. If the tailings piles and waste rock piles in the area were significant sources of sulfate, the evidence for sulfate impact would be unrelated in time to mine shutdown. Further, the impact on wells close to mine workings (and, hence, in proximity to oxidized sulfide concentrations) cannot be explained by the generally centralized locations of mine tailings at the Shullsburg Mine and isolated, scattered locations of waste-rock piles at the Bear Hole Mine. The contribution of such waste-rock piles and tailings basins is unevaluated, but, to the first approximation, these piles and basins do not appear to have a significant impact on ground-water quality, as defined by the investigation to date of private water-supply wells in the Shullsburg area. Runoff from these piles may affect surface-water quality, but this potential has not been evaluated in this study.

Oxidation of Sulfide Minerals

In general, the oxidation of a sulfide mineral can be expressed as:



where X = metal cation (for example, zinc, lead, or iron),
 S = sulfur, and
 O = oxygen.

However, the relationship is certainly more complex and is better represented by a series of equations (Krauskopf, 1967):



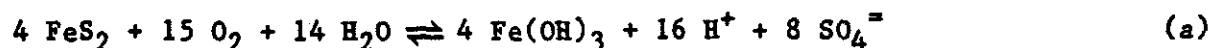
where X^{++} = some metal cation,
 H^+ = hydrogen ion,
 HCO_3^- = bicarbonate ion, and
 CO_2 = carbon dioxide.

These equations are useful in that the role of water is seen to be that of a catalyst, with the mild carbonic acid (H_2CO_3) formed and then attacking the sulfide mineral. The generation of acid water is expected (see equation c), yet that acidity is buffered by the bicarbonate, HCO_3^- , present (equation e). The metal sulfates are much more soluble than their metal sulfide counterparts. Thus, one would expect to see a water solution that is elevated in X (metal) and SO_4 (sulfate) ions.

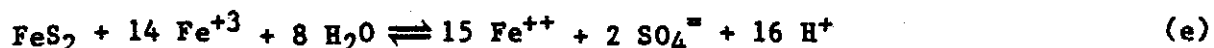
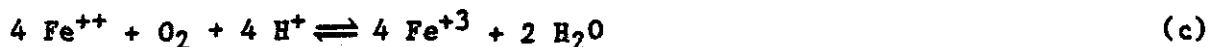
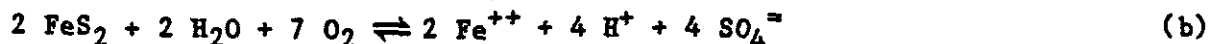
In summary, the subsurface oxidation of metal sulfide minerals should yield a ground water characterized by elevated levels of SO_4 and the metal ions. The acidic conditions of low pH (high H^+ concentration) that might be expected should not appear before the natural buffering capacity of the system, represented by the HCO_3^- , is virtually consumed. In a dominantly carbonate-rock aquifer, the generation of acidic waters is mitigated by the abundance of carbonate and bicarbonate ions available to interact with the water. See the section on Other Investigations of Similar Problems for a discussion of acid-generation potential in a carbonate-rock terrane.

Oxidation of Iron Sulfide

Oxidation of iron sulfide minerals is believed to be the "trigger" mechanism for the generation of high-sulfate, acidic waters and the attack on surrounding minerals which tends to release other constituents into the water. Barnes and Clarke (1964) indicate that the oxidation of the pyrite and marcasite is generalized as:



Looking at this general reaction as a series of reactions, the reactions appear to be (after Stumm and Morgan, 1970, p. 540):



The presence of oxygen can be viewed as important initially but, later it is Fe^{+3} that attacks the marcasite and pyrite to yield still more Fe^{++} , SO_4^{--} , and hydrogen ions. Thus, the oxidation process appears to proceed without the need to have a generally oxygen-rich environment. Further, the equations show that the oxidation of the marcasite generates relatively large quantities of hydrogen ion, in other words, this reaction series is a strong acid-generating series.

It is proposed that oxidation of marcasite and pyrite put iron and sulfate in solution and lowered the water pH. These waters then reacted with the surrounding rocks and minerals, yielding elevated levels of calcium and magnesium (from the dolomite host rock), and elevated levels of zinc from the breakdown of sphalerite ($\text{ZnS} + 2 \text{H}^+ \rightleftharpoons \text{Zn}^{++} + \text{H}_2\text{S}$). Iron in solution would, of course, be expected to increase as the pyrite and marcasite are oxidized. (Preliminary iron data certainly indicate an increase, but the sampling and handling factors mentioned previously do not permit a precise evaluation of the increase and the complicated nature of iron chemistry further inhibits any definitive understanding of the iron content in the ground waters sampled in this investigation.) Based on the general reactions described previously, it is expected that nearly all major constituents would show an increase in concentration. Reflecting the abundance of carbonate rock available, the acidic waters generated by iron sulfide oxidation is buffered by the HCO_3^- anions, yielding pH values in the neutral range. A corollary to the preceding statement is that if the buffering capacity is lost, the waters would remain acidic. The future impact of acidic ground water on well casing in the Shullsburg area or on surface-water quality at points of intersection of the water table with the land surface and surface-water bodies deserves further evaluation. The phenomenon of acidic waters from a carbonate terrane has been documented in the Picher Field in northeastern Oklahoma. See the following section in this report.

OTHER INVESTIGATIONS OF SIMILAR GROUND-WATER PROBLEMS

Has the problem observed in the Shullsburg area been observed before--either within the Upper Mississippi Valley District or in other, geologically-similar mining districts? The answer appears to be "yes" in both instances. Within the Upper Mississippi Valley District, oxidation of sulfide minerals may have accounted for the degraded water quality described in the vicinity of the Graham Mine and Mill in northern Illinois in the late 1960's. Further, water quality associated with flooded mine workings in the Tri-State District (Oklahoma-Missouri-Kansas) is strikingly similar to water quality observed in the sulfate-impacted ground water near Shullsburg; proposed causes of the observed water quality in the mines in the Tri-State District generally parallel those proposed in the Shullsburg area. The former instance (Graham Mine and Mill) suggests that Shullsburg phenomena do have a precedent within rocks and mineral deposits virtually identical to those west and south of Shullsburg. In the latter example (Tri-State District), subsequent surface-water impacts from impacted ground water discharging at the surface suggests further study is needed in the Shullsburg area to determine if additional water-quality problems are still to come.

Graham Mine and Mill

Lindorff and Cartwright (1977) briefly summarize "Case History 105", an example of ground-water contamination resulting, supposedly, from the disposal of ore-processing waste water into an abandoned mine. Walker (1973) also summarized the facts in this situation, based on his own previous investigation (Walker, 1969; report not available for examination) and the investigations in 1968 by the Illinois State Department of Public Health. It is not within the scope of this report to review in detail the information available from the Graham Mine and Mill incident, but a brief summary follows.

The Graham Mine was opened in late 1947 and, due to mine development of zinc-lead ore bodies beneath the water table, pumping was necessary to keep the mine workings relatively free of water. The mine (and associated mill) was operated until January 1966. By that time, a cone of depression had developed due to the drawdown of ground-water levels in and about the mine-dewatering pumps. Several wells within about a mile radius had to be deepened due to water-level declines resulting from the dewatering. Following mine shutdown, pumps were no longer operated and the mine workings (and associated cone of depression) began to fill with ground water. The Graham Mill continued to operate, processing ores from nearby mines.

Graham Mill effluent was typically discharged into the Galena River. Prior to January 1966, mill effluent was mixed with ground water pumped from the Graham Mine. After January 1966 and the closing of Graham Mine, the effluent from the mill was discharged without dilution, and subsequent pollution of the stream developed which resulted in orders from the Board of Public

Health to cease discharge into the Galena River. From the time of the orders (April, 1966), the mill effluent was discharged back into the Graham Mine, that had begun to fill with water four months earlier. Private water-supply wells experienced deteriorating water quality and, following well-owner complaints, an investigation ensued in mid-1968.

The cause of adverse water quality in private wells near the abandoned Graham Mine was postulated as either oxidation of sulfide minerals or the effect of mill effluent discharge into the Graham Mine. Water analyses made at the mine offered no conclusive evidence for either postulated cause. Mr. Robert Bergstrom of the Illinois State Geological Survey (Bradbury and Bergstrom, 1969) referred to the Walker investigation in 1969 as indicating evidence for the mill effluent as the cause of well contamination, but raised general questions based on his own observations and those of James C. Bradbury (also of the Illinois State Geological Survey) concerning the feasibility of mill effluent being the source of pollution especially considering hydrologic gradients in the area. Bradbury seems to indicate that oxidation of sulfide minerals present in dewatered crevices (that were subsequently inundated by rising ground-water levels) is the cause of the well contamination. He further indicates that the rate of water pumping from the abandoned mine into the mill for process-water nearly balances the discharge of the mill effluent back into the mine, thus suggesting that movement of effluent-impacted ground water away from the mine was not likely to have resulted in the contamination in the time involved.

No definite conclusions can be drawn from the information available on the Graham Mine and Mill incident in 1968. However, the role of sulfide oxidation is clearly suggested.

Tri-State District: Picher Field

The Tri-State District began development before 1850 with the Picher Field undergoing initial development in the early 1900's. Following World War I, the Picher Field became the dominant metal producer in the district. The Tri-State District was one of the world's major mining districts and Picher Field has accounted for over 60 percent of the total production of zinc-lead concentrate from the district (Brockie and others, 1968).

Sphalerite and galena mineralization occurs in predominantly replacement-type ore bodies, along with the iron sulfides, marcasite and pyrite, and other gangue minerals such as calcite, dolomite, chalcopyrite, enargite, luzonite and barite. The mineral deposits occur in carbonate host rock that is commonly fractured, especially in mineralized areas. The host rock is known as the Boone Formation of Mississippi age. The mine workings, largely abandoned in the mid-1950's though minor development continued into the 1970's, ranged from about 100 feet to 550 feet below the land surface.

Upon mine shutdown, the mines began to fill with water as the pumps were shut off. Reed and others (1955, p. 136) predicted: "Metallic sulfides of no value will be left in the mines, and will have been oxidized through exposure to air while the mines were pumped free of water. The water that comes in contact with the oxidized sulfides will become acidic." Reed was concerned with generation of acidic water and subsequent investigation has verified his far-sighted concern for water quality.

The U.S. Geological Survey conducted investigations of the water quality within the abandoned mines of the Picher Field (Playton and Davis, 1977; Playton, Davis, and McClafflin, 1978 and 1980) and the water quality in mines and in surface waters fed by mine-water discharge and runoff from tailings piles in the Joplin, Missouri area of the Tri-State District (Barks, 1977). The Joplin area investigation indicated water in abandoned mines had significantly elevated concentrations of sulfate, calcium, and zinc, as well as elevated values for dissolved solids, nickel, manganese, iron, hardness, and electrical conductance. Wells located in or near mine workings appear to be adversely affected. Barks concluded that "...shallow well sampling indicates that there is not widespread movement of highly mineralized mine water in the shallow aquifer". However, the possible contamination of deeper aquifers due to downward gradients was postulated. Surface-water impacts were observed where mine water discharged at the land surface. Tailings runoff has had significant effect on Center and Turkey Creeks where low-pH tailings runoff--high in calcium, sulfate, and zinc--has resulted in a ten-fold increase in dissolved zinc and 25-fold increase in zinc and lead in the bottom sediment.

Sampling of water in seven abandoned mine shafts in the Picher Field was completed initially to characterize water quality with respect to possible use of the water (Playton and Davis, 1977). The water was determined to be unsuited under any conditions for use as a public water supply and would require extensive treatment before being used for any other purpose (Playton, Davis, and McClafflin, 1978 and 1980).

The water in the mine shafts was stratified with pH decreasing, and electrical conductance, temperature, and dissolved solids increasing with sampling depth. Analyses of mine water showed significantly poor water quality with high values of aluminum, cadmium, calcium, dissolved solids, total hardness, iron, lead, manganese, sulfate, specific conductance, and zinc.

The U.S. Geological Survey investigations in the mid-to-late 1970's in the Picher Field area indicated the potential for future adverse impact on surface-water quality. Discharge to the surface regime began in November, 1979 (Adams, 1980). Adams reported on an initial investigation undertaken to assess the extent of surface-water pollution. This investigation indicated that mine discharge into Tar Creek and an artesian spring fed by mine water were adversely affecting the creek and suggested further study to identify mine discharges, and the in-stream water quality in Tar Creek.

By January of 1982, Hittman Associates, Inc. concluded their assessment of surface- and ground-water contamination in the Picher Field, pursuant to a contract with the Oklahoma Water Resources Board. The Hittman report (p. V-1) states:

"Mining activities exposed sulfide bearing minerals to moist, oxygen-rich air which oxidized the iron sulfide minerals. Pyrite-rich waste rock was discarded in mined out portions of drifts, with other sources of waste rock derived from sections of the shaley roof rock present in several mines. These rocks provided additional supplies of pyrite for oxidation.

The cone of depression began filling via natural recharge through the Boone Formation and by direct surface inflow through abandoned shafts, collapsed features and drill holes. The water recharging the mine workings came in contact with the oxidation products that had formed earlier and dissolution occurred rapidly. Initially, the acidic water containing high concentrations of heavy metals reacted with the carbonate host rock. This reaction neutralized some of the acid water and raised the pH to the 4 to 5 range. Eventually, the calcium carbonate host rock lost its neutralizing capacity as precipitates of the reaction formed on the surface area of the carbonate rock... Subsequently, acid neutralization ceased or was reduced greatly. Filling of the cone of depression continued with time. Recharge to the cone was occurring radially and by recharge from infiltrating surface runoff. Therefore, there was no potential for the highly mineralized water to move out of the mining district except downward along the hydraulic gradient toward [an underlying aquifer]. The majority of the mineralized water was confined to the approximate area where it was formed until the water level in the Boone had reached equilibrium."

This extensive quotation from the Hittman report has been included because it indicates a situation generally similar to the situation believed to be present in the Shullsburg area. The report goes on to indicate that eventual recovery of the water quality in the ground-water regime will depend on the processes of dispersion, adsorption and precipitation that will reduce heavy metals concentrations and the dilution of the impacted water in the vicinity of the mine by clean water moving into the area from the upgradient portions of the Boone Formation.

The effect of these impacted ground waters on surface-water quality is projected to be an eventual decline in pH, increase in dissolved solids, and increases in metal concentrations for cadmium, iron, lead, and zinc. The potential for acid mine drainage in Tar Creek is evaluated.

The Hittman report goes on to evaluate abatement options, a discussion of which is beyond the scope of this report.

CONCLUSIONS

The following conclusions are reached regarding the effect of recent mine closings on ground-water quality and quantity in the Shullsburg area:

1. The development of the Shullsburg and Bear Hole Mines complexes required the pumping of large volumes of ground water. The removal of water created extensive areas of unsaturated rock strata, some of which was mineralized with sulfide minerals. Removal of the ground water, which lowered water levels in the area, required the deepening of several wells into the stratigraphically lower St. Peter Sandstone aquifer.

2. The development of the "dewatered" rock or cone of depression in the Galena-Platteville aquifer in the vicinity of the mining areas resulted in oxidation of sulfide minerals, principally iron sulfide minerals (marcasite and pyrite).

3. Iron sulfide oxidation produced sulfate minerals that were soluble and, upon closing of mines and shutdown of water pumps, water levels rose and these soluble sulfate minerals were put into solution in the ground water in the general vicinity of the mines within areas previously unsaturated.

4. Analyses of waters collected from sources within the cone of depression indicate the presence of water high in sulfate, calcium, magnesium, and other parameters. Neutral pH values indicate extensive buffering of the acidic waters generated by the oxidation process. General water quality in the Galena-Platteville aquifer in the Shullsburg and Bear Hole Mines areas has been markedly degraded. Reestablishment of downward-vertical hydrologic gradients may locally pose a threat to St. Peter Sandstone water quality.

5. Well construction appears to have controlled, to some extent, whether or not a particular water-supply well was impacted by sulfate-laden water. The reestablishment of vertically downward hydrologic gradients indicates that even well construction designed to inhibit contact with Galena-Platteville water may not avoid contact with sulfate-laden waters carried down into a lower aquifer along local channels open to water movement.

6. Nothing inherent in the mining process itself appears to have provided a means to avoid the water-quality problem observed in the Shullsburg area. Only the continuance of pumping to maintain the during-mining ground-water conditions could have provided some means of avoiding the existing condition.

RECOMMENDATIONS

The following recommendations are made to the Lafayette County Board of Supervisors with respect to the effects of recent mine closing on ground-water quality and quantity in the Shullsburg area:

1. Continuing investigation of the water quality impact in the Shullsburg and Bear Hole Mine areas is necessary to: (a) monitor potentially changing ground-water quality, (b) establish the trends in recovering water levels, and (c) sample area surface-water quality to develop baseline data.

Ground-water quality in the Galena-Platteville and St. Peter Sandstone aquifers should be monitored over the next several years to evaluate changes in quality, such as a decline in pH. The production of acidic ground water in the Shullsburg and Bear Hole Mine areas is possible despite the carbonate host rock. This possibility poses a threat to the integrity of metal well casings and to surface waters that are fed by ground-water sources originating in this general region.

Water-level measurements should be made on a regular basis to determine the expected directions of ground-water flow and the potential for movement of impacted ground and surface waters into areas previously showing no effect.

Surface waters of the area should be sampled regularly to monitor existing and potentially changing surface-water quality. Surface water fed in part by ground water derived from the Shullsburg and Bear Hole Mine areas may show degraded water quality. Baseline data collection may prove useful for identifying changes in water quality.

2. The Lafayette County Board of Supervisors should carefully review future mine development proposals within the county with a view to ensuring that such proposals consider potential adverse impacts on ground-water quality and quantity so that the public's rights in such waters are reasonably protected. For this purpose, Lafayette County should formally participate in any official proceedings resulting from proposed mine developments, including the master hearing (s. 144.836, Wis. Stats.). As a condition attached to any future metallic mine permit granted in the county by the State of Wisconsin, Lafayette County should specifically request that any private or public wells constructed or re-constructed as a result of dewatering of rock in and about any proposed mine area be designed to prevent movement of potentially impacted ground and surface waters into the new well.

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APPENDIX A
RESULTS OF WATER ANALYSES

NAME: KAMMIES

LOCATION: NE 1/4 sec. 9, T. 1 N., R. 2 E.

#1 (Old well - impacted, new well has been drilled)

Date	Field pH	Conductance (microhos)	Field temperature (°C)	Total solids (g/l) ¹	Chloride (Cl) (ppm)	Lab pH	Total alkalinity as CaCO ₃ (mg/l) ²	Arsenic (As) (ug/l) ³	Cadmium (Cd) (ug/l)	Lead (Pb) (ug/l)	NO ₂ - NO ₃ as Nitrogen (mg/l)	Sulfate (SO ₄) (mg/l)	parts per million (ppm)												Total residue (mg/l)	Samples Taken By
													Phosphate (P)	Potassium (K)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Copper (Cu)	Iron (Fe)	Aluminum (Al)	Zinc (Zn)	Manganese (Mn)	Boron (B)	Sulfur (S)		
9/24/80								130		4200		1400			340	250		< .05	65		22	1.40			3012	DNR
10/10/80								< 10		90		1800			598	285		< .05	20		22	1.62			1408	DNR
10/24/80					35			< 10		86		1700			435	290		< .05	20		22	1.78			3362	DNR Raw water
10/24/80					4			< 10		< 3		1700			33	7		< .05	1.4		2.9	0.11			3208	DNR Treated water
11/24/80								< 10							64	34			0.4		8.9	0.04			328	DNR New well
12/11/80								< 10							64	33			0.9		0.38	0.04			304	DNR
6/ 4/81								< 10	< 0.2	< 3			0.22	1.40	58.1	31.5	3.22	< 0.01	0.05	0.35	0.07	0.01	0.04	6.32	WG&NHS	
12/22/81	7.3	350	11.0	0.49	0.35	7.3	241	< 10	< 0.2	< 3	< 0.5	18	0.22	0.62	59.6	32.1	1.97	< 0.01	0.04	0.35	0.04	0.01	0.04	6.56	WG&NHS	
2/24/81						7.6	276	< 10	< 0.2	< 3		19			60	33			0.7		0.15	0.04			290	DNR
6/ 1/82		365	12.0	0.50	0.71	7.7	271	< 10	< 0.2	< 3	< 0.5	18	0.22	0.62	61.0	33.0	3.62	< 0.01	0.04	0.35	0.03	0.01	0.31	6.84	WG&NHS	
12/22/82		335	9.0	0.51	0.31	7.6	214	< 10	< 0.2	< 3	< 0.5	18	0.22	0.62	56.5	32.6	2.36	< 0.01	0.04	0.35	0.02	0.01	0.08	6.84	WG&NHS	
															</											

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(ug/l) = micrograms per liter

NAME: ESPENSCHIED/TROXEL

LOCATION: SW 1/4 sec. 9, T. 1 N., R. 2 E.

#2 (Impacted well)

Date	Field pH	Conductance (micromhos)	Field temperature (°C)	Total solids (g/l) ¹	Chloride (Cl) (ppm)	Lab pH	Total alkalinity as CaCO ₃ (mg/l) ²	Arsenic (As) (ug/l) ³	Cadmium (Cd) (ug/l)	Lead (Pb) (ug/l)	NO ₂ - NO ₃ as Nitrogen (mg/l)	Sulfate (SO ₄) (mg/l)	parts per million (ppm)												Total residue (mg/l)	Samples Taken By
													Phosphate (P)	Potassium (K)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Copper (Cu)	Iron (Fe)	Aluminum (Al)	Zinc (Zn)	Manganese (Mn)	Boron (B)	Sulfur (S)		
1/27/81						7.2	386	< 10	13.0	250		1225			315	189		< 0.05	10.5		8.60	0.96			2294	DNR
6/ 4/81								< 10	2.8	120			0.22	2.80	366	197	15.1	0.03	5.20	1.41	3.13	0.75	0.35	402		WG&NHS
10/27/81	6.9	1650	10.0					< 10	0.4	29	< 0.5	1600														WG&NHS

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(ug/l) = micrograms per liter

NAME: BRUUN

LOCATION: SP. SE, sec. 21, T. 1 N., R. 2 E.

#5 (Old well - impacted, new well has been drilled)

New well

Date	Field pH	Conductance (micromhos)	Field temperature (°C)	Total solids (g/l) ¹	Chloride (Cl) (ppm)	Lab pH	Total alkalinity as CaCO ₃ (mg/l) ²	Arsenic (As) (ug/l) ³	Cadmium (Cd) (ug/l)	Lead (Pb) (ug/l)	NO ₂ - NO ₃ as Nitrogen (mg/l)	Sulfate (SO ₄) (mg/l)	parts per million (ppm)												Total residue (mg/l)	Samples Taken By
													Phosphate (P)	Potassium (K)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Copper (Cu)	Iron (Fe)	Aluminum (Al)	Zinc (Zn)	Manganese (Mn)	Boron (B)	Sulfur (S)		
7/21/80					17	7.4	464					2800							1.8		1.30			4886	DNR	
9/24/80	7.2					7.2	471	< 10	1.1	< 3		2650			380	480	< 0.05	5.4		3.50	0.72			4924	DNR	
10/10/80						7.3	472	< 10	1.0	< 3		2800			551	525	< 0.05	8.0		2.94				5264	DNR	
1/14/81					8	8.1	282	86	< 0.2	7		800			192	157	260	< 0.05	4.4		2.10	0.33		1502	DNR New well	
2/14/81								47		< 3		240												503	DNR	
2/24/81													< 0.22	1.34	90.0	61.8	2.24	< 0.01	0.05	< 0.35	0.22	0.08	0.07	65.4	WG&NHS	
6/ 4/81				0.31				22	0.4	47			< 0.22	2.62	63.5	40.1	4.67	0.02	0.25	0.47	0.20	0.04	0.05	23.1	WG&NHS	
10/27/81	7.1	396	12.0			7.1		< 10	< 0.2	< 3	< 0.5	27													WG&NHS	
12/22/81	7.3	370	11.0	0.44	1.07	7.5	238	< 10	< 0.2	< 3	< 0.5	14	< 0.22	< 0.62	56.9	32.4	1.68	< 0.01	< 0.01	< 0.35	0.05	0.02	0.04	4.94	WG&NHS	
2/24/82						7.5	272	< 10	< 0.2	7		13			58	33					0.57	0.04			274	DNR
6/ 1/82		368	11.7	0.57	0.79	7.4	275	< 10	< 0.2	< 3	< 0.5	12	< 0.22	0.71	58.7	33.1	3.41	< 0.01	0.02	< 0.35	0.10	0.02	0.06	4.43	WG&NHS	
12/22/82		349	10.0	0.54	0.31	7.7	233	< 10	< 0.2	< 3	< 0.5	11	< 0.22	0.62	57.7	32.4	2.03	< 0.01	< 0.01	< 0.35	0.05	0.02	0.04	4.44	WG&NHS	
																									</	

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(ug/l) = micrograms per liter

NAME: EUSTICE/McCORD

LOCATION: SW 1/4 sec. 28, T. 1 N., R. 2 E.

#6 (Old well - impacted) #24 (New well)

New well

Date	Field pH	Conductance (micromhos)	Field temperature (°C)	Total solids (g/l) ¹	Chloride (Cl) (ppm)	Lab pH	Total alkalinity as CaCO ₃ (mg/l) ²	Arsenic (As) (ug/l) ³	Cadmium (Cd) (ug/l)	Lead (Pb) (ug/l)	Mn ²⁺ - NO ₃ ⁻ as Nitrogen (mg/l)	Sulfate (SO ₄) (mg/l)	parts per million (ppm)												Total residue (mg/l)	Samples Taken By
													Phosphate (P)	Potassium (K)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Copper (Cu)	Iron (Fe)	Aluminum (Al)	Zinc (Zn)	Manganese (Mn)	Boron (B)	Sulfur (S)		
9/24/80	7.1					6.8	430	< 10	0.9	25		2325			380	450	< 0.05	6.8		9.70	1.10			4662	DNR	
6/ 4/81				3.50				< 10	1.2	81			< 0.22	4.46	515	340	8.76	0.04	0.72	1.57	7.23	0.88	0.44	720	WG&NHS	
10/27/81	6.7	2680	12.5					< 10	1.3	76	< 0.5	3333													WG&NHS	
12/22/81	6.7	2110	11.0	3.24	12.0	7.2	305	< 10	0.3	13	< 0.5	1700	< 0.22	4.14	495	279	6.14	< 0.01	0.53	0.43	12.1	0.87	0.22	613	WG&NHS New well	
2/10/82						7.0	320	< 10	< 0.2	< 3	< 0.5	1900			430	270	< 0.05	36		15.0	0.92			3262	DNR	
2/24/82						6.8	320	< 10	0.4	< 3		2000			400	270				16.0	0.88			3244	DNR	
6/ 1/82		2320	12.1	3.30	12.0	6.9	316	< 10	< 0.2	< 3	< 0.5	1700	< 0.22	< 0.62	421	282	18.2	< 0.01	0.07	3.35	8.29	0.99	< 0.03	631	WG&NHS	
12/22/82		2050	7.8	1.98	13.1	6.7	287	< 10	0.3	< 3	< 0.5	1900	< 0.22	< 0.62	442	327	6.86	< 0.01	0.04	1.05	2.96	1.08	0.14	705	WG&NHS	

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(ug/l) = micrograms per liter

NAME: HOCKING

LOCATION: NE 1/4 sec. 28, T. 1 N., R. 2 E.

#7 (Old well - impacted, new well has been drilled)

New well

Date	Field pH	Conductance (micromhos)	Field temperature (°C)	Total solids (g/l) ¹	Chloride (Cl) (ppm)	Lab pH	Total alkalinity as CaCl ₂ (mg/l) ²	Arsenic (As) (μg/l)	Cadmium (Cd) (μg/l)	Lead (Pb) (μg/l)	NO ₂ - N ₃ as Nitrogen (mg/l)	Sulfate (SO ₄) (mg/l)	parts per million (ppm)												Total residue (mg/l)	Samples Taken By
													Phosphate (P)	Potassium (K)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Copper (Cu)	Iron (Fe)	Aluminum (Al)	Zinc (Zn)	Manganese (Mn)	Boron (B)	Sulfur (S)		
9/24/80	6.8					7.2	374	< 10	< 0.2	< 3		875			280	140		< 0.05	6.0		1.50	0.28		1956	DNR	
10/24/80					9	7.0	366	< 10	< 0.2	12		900			325	148	6	< 0.05	6.9		4.35	0.33		1968	DNR	
1/27/81						7.3	328	23	< 0.2	7		425			170	88		< 0.05	1.6		0.94	0.12		1042	DNR New well	
2/24/81				0.76									< 0.22	1.99	146	71.3	4.54	< 0.01	0.02	< 0.35	0.45	0.10	0.09	112	WG&NHS	
6/ 4/81				0.42				< 10	< 0.2	5			< 0.22	2.91	93.9	47.9	6.75	0.03	0.12	0.74	0.33	0.05	0.11	50.1	WG&NHS	
12/22/81	7.4	387	12.0	0.48	0.73	7.6	245	< 10	< 0.2	< 3	< 0.5	10	< 0.22	0.62	61.6	33.6	2.27	< 0.01	0.01	< 0.35	0.07	0.01	0.03	9.64	WG&NHS	
2/24/82						7.6	276	< 10	< 0.2	17		25			61	34					< 0.04	0.17		286	DNR	
6/ 1/82		385	12.5	0.53	0.64	7.5	248	< 10	< 0.2	5	< 0.5	18	< 0.22	0.75	59.2	33.6	3.82	< 0.01	< 0.01	< 0.35	0.01	0.01	0.05	6.70	WG&NHS	
12/22/82		361	10.0	0.49	0.24	7.8	235	< 10	< 0.2	< 3	< 0.5	12	< 0.22	0.62	0.38	0.10	142	< 0.01	0.01	< 0.35	0.02	< 0.01	< 0.03	4.09	WG&NHS	

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(ug/l) = micrograms per liter

NAME: GENSLEY

LOCATION: NW 1/4 sec. 27, T. 1 N., R. 2 E.

#8 (Old well - impacted, new well has been drilled)

Date	Field pH	Conductance (micromhos)	Field temperature (°C)	Total solids (g/l) ¹	Chloride (Cl) (ppm)	Lab pH	Total alkalinity as CaCO ₃ (mg/l) ²	Arsenic (As) (ug/l) ³	Cadmium (Cd) (ug/l)	Lead (Pb) (ug/l)	NO ₂ - NO ₃ as Nitrogen (mg/l)	Sulfate (SO ₄) (mg/l)	parts per million (ppm)												Total residue (mg/l)	Samples Taken By
													Phosphate (P)	Potassium (K)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Copper (Cu)	Iron (Fe)	Aluminum (Al)	Zinc (Zn)	Manganese (Mn)	Boron (B)	Sulfur (S)		
9/24/80	7.3					7.2	314	< 10	1.7	25		425			160	34		<0.05	2.0		11.0	0.26		1134	DNR	
11/10/80					4	7.4	310	< 10	1.3	22		600			240	103		< 0.05	10		16.0	0.40		1448	DNR	
12/11/80					3	7.0	314	< 10	1.6	14		800			260	121		< 0.05	6.6		14.0	0.04		1646	DNR	
6/ 4/81				1.44				< 10	0.6	20			<0.22	3.54	253	118	6.74	0.03	2.26	0.90	8.92	0.32	0.20	262	WG&NHS	
12/22/81	7.3	347	10.0	0.47	0.35	7.5	240	< 10	<0.2	< 3	<0.5	14	<0.22	0.62	56.3	32.1	1.92	<0.01	0.01	<0.35	0.26	0.01	0.03	4.88	WG&NHS New well	
2/24/82						7.5	276	< 10	<0.2	< 3		11			56	33			0.80		0.64	<0.04		282	DNR	
6/ 1/82		362	11.8	0.57	0.56	7.9	259	< 10	<0.2	< 3	<0.5	11	<0.22	0.96	58.9	34.4	3.62	<0.01	0.02	<0.35	0.26	0.01	<0.03	5.94	WG&NHS	
12/22/82		331	10.0	0.30	0.24	7.8	236	< 10	<0.2	< 3	<0.5	12	<0.22	0.62	56.5	32.6	2.43	<0.01	0.01	<0.35	0.07	0.01	<0.03	4.77	WG&NHS	
										</																

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(ug/l) = micrograms per liter

NAME: GENSLE/EDGE

LOCATION: SP/SM sec. 22, T. 1 N., R. 2 E.

#9 (Old well - impacted, new well has been drilled)

Date	Field pH	Conductance (microhos)	Field temperature (°C)	Total solids (g/l) ¹	Chloride (Cl) (ppm)	Lab pH	Total alkalinity as CaCO ₃ (mg/l) ²	Arsenic (As) (ug/l)	Cadmium (Cd) (ug/l)	Lead (Pb) (ug/l)	NO ₂ - NO ₃ as Nitrogen (mg/l)	Sulfate (SO ₄) (mg/l)	Parts per million (ppm)											Total residue (ug/l)	Samples Taken By
													Phosphate (P)	Potassium (K)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Copper (Cu)	Iron (Fe)	Aluminum (Al)	Zinc (Zn)	Manganese (Mn)	Boron (B)	Sulfur (S)	
9/25/80	7.4					6.9	416	< 10	0.5	< 3		3500			370	820		< 0.05	11		5.00	1.70		6994	DNR
6/4/81								< 10	0.2	< 3			< 0.22	< 0.62	459	804	11.7	0.01	2.56	1.99	1.87	0.88	0.74	1200	WG&NHS
12/22/81	6.4	1800	12.0	6.64	32.6	7.6	371	< 10	0.3	16	2.8	3400	< 0.22	< 0.62	427	896	17.2	< 0.01	0.10	1.61	0.97	0.38	0.44	1130	WG&NHS
2/10/82						7.7	274	11	< 0.2	< 3		19			58	34		< 0.01	2.4		2.00	0.04		300	DNR New well
6/1/82		380	13.2	0.56	0.49	7.5	264	< 10	< 0.2	< 3	< 0.5	12	< 0.22	0.65	57.9	32.3	3.75	< 0.01	0.01	< 0.35	0.25	0.01	< 0.01	4.88	WG&NHS
12/22/82		140	10.0	0.50	0.31	7.8	253	< 10	< 0.2	< 3	< 0.5	10	< 0.22	< 0.62	58.4	33.1	2.74	< 0.01	0.01	< 0.35	0.17	0.02	< 0.01	4.37	WG&NHS

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(ug/l) = micrograms per liter

NAME: COOLIDGE/HATFIELD

LOCATION: SP/SM sec. 16, T. 1 N., R. 2 E.

#23 (Coolidge Well - impacted) #10 (Hatfield - new well)

Date	Field pH	Conductance (microhos)	Field temperature (°C)	Total solids (g/l) ¹	Chloride (Cl) (ppm)	Lab pH	Total alkalinity as CaCO ₃ (mg/l) ²	Arsenic (As) (ug/l)	Cadmium (Cd) (ug/l)	Lead (Pb) (ug/l)	NO ₂ - NO ₃ as Nitrogen (mg/l)	Sulfate (SO ₄) (mg/l)	Parts per million (ppm)											Total residue (ug/l)	Samples Taken By
													Phosphate (P)	Potassium (K)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Copper (Cu)	Iron (Fe)	Aluminum (Al)	Zinc (Zn)	Manganese (Mn)	Boron (B)	Sulfur (S)	
#23 11/10/80					40	7.5	349	< 10	2.2	< 3		1200			256	238						0.09		2340	DNR #23
#23 12/11/80					40	7.7	362	< 10	2.1	< 3	< 0.5	1300			270	258		< 0.05	0.07		3.80	0.10		2504	DNR #23
#23 1/14/81					45	8.0	368	< 10	5.4	< 3		1200			252	248		< 0.05	0.01		17.3	0.11		2310	DNR #23
#23 6/4/81			1.93					< 10	1.5	< 3			< 0.22	5.32	215	199	17.4	0.02	0.08	0.92	4.04	0.13	0.23	328	WG&NHS #23
#23 12/22/81	6.7	2000	8.0	3.28	67.5	7.5	337	< 10	6.6	14	1.6	1600	< 0.22	2.25	372	351	10.3	< 0.01	0.04	0.53	7.74	2.41	0.20	586	WG&NHS #23
#23 12/22/81	7.4	349	11.0	0.48	0.73	7.6	245	< 10	< 0.2	< 3		23	< 0.22	1.70	58.4	33.6	2.20	< 0.01	0.01	< 0.35	0.02	0.04	0.03	4.18	WG&NHS #10
#10 2/24/82						7.8	284	< 10	< 0.2	< 3		10			60	34			3.1		0.04	< 0.01		310	DNR #10
#10 6/1/82		372	11.5	0.54	0.79	7.1	262	< 10	< 0.2	< 3	< 0.5	9	< 0.22	1.55	59.4	33.9	3.71	< 0.01	0.02	< 0.35	0.04	0.03	0.03	3.79	WG&NHS #10
#23 6/1/82		1850	11.8	2.4	54.6	7.0	346	< 10	4.1	< 3	1.0	1300	< 0.22	< 0.62	275	225	34.1	< 0.01	0.08	< 0.35	4.69	1.10	< 0.03	416	WG&NHS #23
#10 12/22/82		363	10.0	0.58	4.21	8.11	244	< 10	< 0.2	< 3	0.5	8.9	< 0.22	< 0.62	60.9	33.8	2.02	< 0.01	0.01	< 0.35	0.04	< 0.01	< 0.03	3.68	WG&NHS #10
#23 12/22/82		2480	8.0	4.75	72.3	7.6	315	< 10	21	< 3	4.9	2300	< 0.22	< 0.62	498	432	34.3	< 0.01	0.05	1.22	3.65	2.17	0.15	862	WG&NHS #23

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(ug/l) = micrograms per liter

WIEGEL

LOCATION: Center sec. 2, T. 1 N., R. 2 E.

#11 (Area well)

[illegible]

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(µg/l) = micrograms per liter

NAME: SHULLSBURG CITY WELL NO. 4

LOCATION: SE-NE 1/4 sec. 10, T. 1 N., R. 2 E.

#12 (Area well)

[illegible]

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(µg/l) = micrograms per liter

LOCATION: SE, SE, sec. 1, T. 1 N., R. 2 E.

#13 (Area well)

[illegible]

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(µg/l) = micrograms per liter

LOCATION: SW 1/4 sec. 13, T. 1 N., R. 2 E.

#14 (Area well)

[illegible]

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(µg/l) = micrograms per liter

NAME: RFES

LOCATION: NE¹/4NW¹/4 sec. 23, T. 1 N., R. 2 E.

#15 (Area w/ 11)

[illegible]

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(ug/l) = micrograms per liter

NAME: RICHARD MARCH

LOCATION: SE 1/4 sec. 26, T. 1 N., R. 2 E.

#16 (Area well)

[illegible]

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(μg/l) = micrograms per liter

LOCATION: SW 1/4 SEC. 22, T. 1 N., R. 2 E.

LOCATION: SW 1/4 SEC. 22, T. 1 N., R. 2 E.

LOCATION: SW 1/4 SEC. 22, T. 1 N., R. 2 E.

LOCATION: SW 1/4 SEC. 22, T. 1 N., R. 2 E.

LOCATION: NE 1/4 sec. 33, T. 1 N., R. 2 E.

LOCATION: NE 1/4 sec. 33, T. 1 N., R. 2 E.

LOCATION: NE 1/4 sec. 33, T. 1 N., R. 2 E.

LOCATION: NE 1/4 sec. 33, T. 1 N., R. 2 E.

NAME: DEPPE

LOCATION: NW 1/4 sec. 29, T. 1 N., R. 2 E.

#19 (Area well)

Date	Field pH	Conductance (microhmhos)	Field temperature (°C)	Total solids (g/l) ¹	Chloride (Cl) (ppm)	Lab pH	Total alkalinity as CaCO ₃ (mg/l) ²	Arsenic (As) (ug/l)	Cadmium (Cd) (ug/l)	Lead (Pb) (ug/l)	NO ₂ - NO ₃ as Nitrogen (mg/l)	Sulfate (SO ₄) (mg/l)	Parts per million (ppm)											Total residue (mg/l)	Samples Taken By
													Phosphate (P)	Potassium (K)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Copper (Cu)	Iron (Fe)	Aluminum (Al)	Zinc (Zn)	Manganese (Mn)	Boron (B)		
9/25/80	7.3					7.3	358	10	<0.2	6		475			130	120			10		0.55	0.22		1300	DNR
10/20/81	7.1			0.86	8.10	7.5	294	<10	<0.2	<1	<0.5	280	<0.22	1.39	99.6	77.9	4.70	<0.01	0.08	<0.35	0.03	0.14	0.04	92.5	WG&NHS
3/12/82		495	10.0	0.58	1.32	7.4	259	<10	<0.2	<1	<0.5	130	<0.22	1.16	81.7	47.6	3.35	<0.01	0.05	<0.35	0.01	0.07	0.04	38.1	WG&NHS
					</																				

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(ug/l) = micrograms per liter

NAME: AWE

LOCATION: SE 1/4 sec. 17, T. 1 N., R. 2 E.

#20 (Area well)

Date	Field pH	Conductance (micromhos)	Field temperature (°C)	Total solids (g/l) ¹	Chloride (Cl) (ppm)	Lab pH	Total alkalinity as CaCO ₃ (mg/l) ²	Arsenic (As) (ug/l)	Cadmium (Cd) (ug/l)	Lead (Pb) (ug/l)	NO ₂ - NO ₃ as Nitrogen (mg/l)	Sulfate (SO ₄) (mg/l)	parts per million (ppm)												Total residue (mg/l)	Samples Taken By
													Phosphate (P)	Potassium (K)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Copper (Cu)	Iron (Fe)	Aluminum (Al)	Zinc (Zn)	Manganese (Mn)	Boron (B)	Sulfur (S)		
9/24/80	7.2					7.3	370	<10	0.8	21		250			110	98		<0.05	2.0		0.44	0.06			810	DNR
10/20/81	7.1			0.81	17.9	7.5	364	<10	1.2	30	4.2	320	<0.22	3.37	135	62.7	17.7	<0.01	0.03	<0.35	0.25	0.04	0.11	80.1		WG&NHS
3/12/82		790	11.0	0.81	17.6	7.5	322	<10	0.8	62	<0.5	280	<0.22	3.05	147	66.8	14.5	<0.01	0.03	<0.35	0.19	0.04	0.11	88.9		WG&NHS
4/30/82		880	11.2					<10	1.5	40	<0.5	220														WG&NHS
6/ 1/82		900	11.5	0.90	20.1	7.3	325	<10	1.8	44	<0.5	320	<0.22	15.3	127	62.6	55.6	0.28	0.37	<0.35	0.09	0.10	<0.03	89.3		WG&NHS

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(ug/l) = micrograms per liter

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LAIRD

LOCATION:

S4545 DEC. 19. T. 1 N., R. 2 E.

#21 (Area well)

[illegible]

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(µg/l) = micrograms per liter

VAMP:

GENSLE/ROGERS

LOCATION:

SW&SW& sec. 21, T. 1 N., R. 2 E.

#22 (Requested sample)

[illegible]

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(µg/l) = micrograms per liter

LOCATION: NE 1/4 sec. 26, T. 1 N., R. 2 E.

#25 (Ruminant similia)

[illegible]

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(µg/l) = micrograms per liter

NAME: REINBOLD

LOCATION: NE¹/NE¹ sec. 10, T. 1 N., R. 1 E.

#26 (Requested sample)

[illegible]

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(µg/l) = micrograms per liter

LOCATION: SLE-SLE, sec. 15, T. 19, R. 2 E

121. (Revised version)

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(ug/l) = micrograms per liter

LOCATION: SE NELSON, sec. 22, T. 1 N., R. 2 E.

#28A (Impacted point)

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(ug/l) = micrograms per liter

SLE:

LOCATION:

428B (impacted point)

[illegible]

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(µg/l) = micrograms per liter

NAME: MINE SHAFT (779 ft. ⁺ 4 ft above sea level)

LOCATION: SE $\frac{1}{4}$ NE $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 22, T. 1 N., R. 2 E.

§28C. (Inserted Point)

[illegible]

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(µg/l) = micrograms per liter

LOCATION: NE1/4SE1/4 sec. 29, T. 1 N., R. 2 E.

#29 (Requested sample)

[illegible]

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(µg/l) = micrograms per liter

NAME: TEASDALE

LOCATION: NW 1/4 sec. 10, T. 1 N., R. 1 E.

#30 (Requested sample)

[illegible]

¹(g/l) = grams per liter; ²(mg/l) = milligrams per liter; ³(µg/l) = micrograms per liter

APPENDIX B

DISCUSSION OF METHODOLOGY

Selection of Sampling Points

The Geological and Natural History Survey study identifies three general types of sources for ground water samples, "sulfate-impacted", "area" and "requested". An impacted sampling source is a well or other sampling point that is open, at least in part, to the Galena-Platteville aquifer, shows sulfate levels above 700 mg/l, and the resident complains of a recent change in water quality such that symptoms that are attributable to high-sulfate-water consumption have appeared. In a few cases, water samples were taken initially as either requested or area samples and the water-quality analyses indicated that ground water collected at these sampling points was sulfate-impacted. There are fourteen sampling points that have been classified as sulfate-impacted wells. Eight new wells have been drilled. Six impacted wells remain available for use by well owners as of this date. The main shaft at the Shullsburg complex has also been sampled and contains impacted ground water. It is not a private water-supply well.

Area sampling sources are non-sulfate-impacted private water-supply wells within the geographical township of the mines (T. 1 N., R. 2 E.). These wells were chosen on the basis of known well construction and the aquifer rock type. Well-construction information, originally submitted to the Wisconsin Department of Natural Resources (DNR), was obtained from well-construction reports on file at the Wisconsin Geological and Natural History Survey (WG&NHS) as well as from the DNR. The authors chose wells for area sampling sources which have only one aquifer as the source of water. The source of the water is either the Galena-Platteville aquifer or the St. Peter Sandstone aquifer. Well-construction reports which indicated that the St. Peter was penetrated but were not cased into the St. Peter were rejected due to the fact that the source of water included both aquifers. There are ten area wells being sampled. Seven of these are Galena-Platteville wells and three are St. Peter wells.

Requested samples are from generally non-sulfate-impacted private water-supply wells sampled after the resident or owner contacted Bruce Dennis (Lafayette County Extension resource agent) to have water samples taken. There have been five requested samples taken at the request of Mr. Dennis and one taken at the request of the Wisconsin DNR for a total of six. One of the requested samples is clearly an impacted well in terms of sulfates. (This well is now included in the impacted wells discussed previously.) One of the remaining requested wells is inconclusive in terms of impact (#22). Two of the requested samples are clearly unrelated to the shutdown of the Shullsburg and Bear Hole Mines by virtue of their long distance from the mines. (These sampling points are not shown on Plate 1 as they are located outside of the

geographical township.) The well sampled at the request of the DNR is close enough to the mine that it should be impacted but has not, as of late 1982, shown impact.¹

Sampling Methodology

Water samples were taken from private water-supply wells and from the main shaft of the Shullsburg Mine complex. Samples from the private water-supply wells were taken from discharge points located as close to the well as possible. The sampling point was usually a barnyard hydrant but in some cases an outside faucet was used. Wherever possible the sample was taken before the water entered the household pressure tank. The hydrants or faucets were opened for a minimum of five minutes with an average of ten minutes. A 2000 millileter (ml) linear polyethylene bottle was rinsed twice with sample water and then filled. The sample was then split into four plastic bottles: one 625 ml and one 250 ml supplied by the State Laboratory of Hygiene and two 500 ml polyethylene bottles, one of which was supplied by the Soil Science Department, University of Wisconsin-Madison, and the other purchased from American Scientific Products. The 250-ml bottle was dosed with 2.5 ml of 35% [8N] nitric acid provided by the State Laboratory of Hygiene. The split samples were placed in an iced cooler for transport to the laboratories. If samples could not be delivered to the laboratories on the day of sampling, they were stored in a refrigerator overnight and delivered the following day.

Field data were collected from a fifth sample bottle. Temperature, pH, and electric conductivity measurements were taken from water collected from a 500-ml bottle. The bottle was placed in a water bath. Temperature and electric conductivity measurements were taken with a Yellow Springs Instrument Model 33 Salinity conductivity and temperature meter. A Lead-Northrup pH-meter was used to measure pH in the field. Some difficulty was encountered while determining pH with this meter. The rather cold temperature of the water (10°-12° C) made it difficult to standardize the meter. The pH electrode also appeared to be malfunctioning. The time needed to get a good pH measurement and the apparent malfunctioning of the probe lead to the abandonment of field pH. For the purposes of the study to date and in light of the meter difficulties, the authors felt that laboratory pH was a sufficient backup to the field data. Lab pH generally was about one or one-half pH unit higher than field pH, reflecting the loss of CO₂, carbon dioxide, during the handling.

Analytical Methodology

Three laboratories--the State Lab of Hygiene, the University of Wisconsin-Madison Soil Science Department "Greenhouse" Lab and the Soil and Plant Analysis Lab, University of Wisconsin-Extension--analyzed the water samples.

¹ See appendix C, Special Cases, the Hendrickson Well for more information.

The State Lab of Hygiene (University of Wisconsin-Madison) provided the 625-ml and the 250-ml bottles and analyzed samples collected in them. Sulfates and nitrates were determined in water collected in the 625-ml bottles. Nitrates were analyzed using an automated colorimetric instrument with the cadmium-column-reduction colorimetric method. The lower detection limit is 0.5 mg/l \pm 0.1. Sulfates were analyzed using a colorimetric instrument following the turbidometric method. The lower detection limit is 4 mg/l \pm 2 mg/l. Lead, cadmium and arsenic were determined in water collected in the 250-ml bottles. The Perkin-Elmer 5000 atomic absorption unit was used. The lower detection limits are 10 μ g/l \pm 3.5 for arsenic, 0.2 μ g/l \pm .26 for cadmium and 3 μ g/l \pm 2.2 for lead.

The Soil and Plant Analysis Lab, University of Wisconsin-Extension, received one set of 500-ml bottles. This lab analyzed for phosphate, potassium, calcium, magnesium, sodium, copper, iron, aluminum, zinc, manganese, boron and sulfur. These twelve parameters are included in the Soil and Plant Analysis Lab's water A program. This program is an automated water analysis process employing a Bausch and Lomb ARL 34000 ICP spectrometer with an associated computer. The method used is spectral emissions analysis. The lower detection limits in ppm are as follows: phosphate (0.212), potassium (0.621), calcium (0.043), magnesium (0.104), sodium (0.496), copper (0.012), iron (0.011), aluminum (0.352), zinc (0.010), manganese (0.003), boron (0.030), and sulfur (0.135). The error at detection limits are \pm 10% and decrease to \pm 1 to 2% as the concentration increases.

The "Greenhouse" Lab (associated with the University of Wisconsin-Madison Soil Science Department) provided the other set of 500-ml bottles and analyzed water samples collected in them. This lab analyzed water samples for total solids, chlorides, lab pH, and total alkalinity. Total solids were determined by drying a portion of the sample in an oven at 110° C. to a constant weight with an error of \pm 5%. A pH meter was used to determine the lab pH of the samples. Total alkalinity was determined using the phenolphthalein alkalinity method². This determination represents total alkalinity because all of the water samples have a pH less than 8.3. Chloride was analyzed using the automated ferricyanide method³.

² STANDARD METHODS for the Examination of Water and Wastewater, 15th edition, 1980. APHA-AWWA-WPCF. Part 403, p. 253.

³ IBID, Part 407 D, p. 275.

APPENDIX C

SPECIAL CASES

The Hendrickson Well (#27)

The Hendrickson well is of special interest because it is reasonably expected to show the adverse impact of high-sulfate water, yet the water quality to date remains good. The residents have not complained of water-quality problems. The well is located in SE $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 15, T. 1 N., R. 2 E. and is located between three ore bodies--Hendrickson, Kittoe, and North Hayden. The well is approximately 325 ft deep with 46 ft of casing. It penetrates about 44 ft into the St. Peter sandstone. Thus, the well has 279 feet of open hole, 235 of which are in the Galena-Platteville aquifer.

There are two factors which may have contributed to the continuing low sulfate levels in the ground water in the area of this well: time and geology. The timing of the mining of 3 nearby ore bodies may be significant. The Hendrickson ore body to the west and the portion of the North Hayden just to the south were mined relatively late in the history of the Shullsburg Mine complex. Thus, the area around the Hendrickson well may have been dewatered for a shorter period of time than some of the other areas. There was thus less time for oxidation of iron sulfides to take place, possibly reducing the amount of sulfate produced, which in turn, would limit the impact of high sulfate levels in the ground water. Time is also involved in the consideration of ground-water velocities. The Hendrickson well is about 500 ft from the nearest ore body. Impacted waters from mineralized zones near the ore bodies may not yet have had enough time to reach the Hendrickson well.

The geology around the well could also be the cause for the slow movement of ground water. The Hendrickson well may have been drilled into a sound rock matrix relative to the rock matrix near an ore body. The drill log of the hole indicates that the limestone of the Platteville is tightly cemented. No crevices are noted in the driller's log. The hole has very little mineralization, with only a few intervals indicating iron sulfides, one of which is currently above the water table. This mineralized interval is 25 feet thick with 3-5% marcasite--ground water encountering this zone could show a change in water quality.

The Eustice/McCord Well (#6, #24)

The Eustice (owner)/McCord (tenant) well is a special case because a new well (#24) has been constructed in supposed accordance with DNR recommendations to replace an older, impacted well (#6) and yet the water quality remains unacceptable. The well is an anomaly with respect to the other new wells which have been constructed in accordance with DNR recommendations and which show excellent water quality. Well construction began in October of 1981 and was finished in December. The original depth of the well was 490

feet with 475 feet of grout and casing. Thirty-five feet of sandstone was penetrated with 15 feet being open hole below the bottom of the casing.

The Survey sampled the new well (#24) on December 22, 1981. The sulfate level of this sample was 1700 mg/l. This is the same order of magnitude of sulfates that the old impacted well (#6) showed. The DNR took samples on February 10 and 24, 1982. The sulfate levels of these samples was 1900 mg/l and 2000 mg/l respectively. This information implies that the St. Peter Sandstone aquifer is being contaminated from the Galena-Platteville aquifer along some path of communication between the two aquifers.

After the February 24th sample results were received, the DNR recommended that the well be pumped for an extended period. The owner complied with this recommendation and the well was pumped for 30 days. No significant change was found in sulfate concentrations after pumping. The DNR next recommended that the well be deepened in an attempt to find acceptable water and to facilitate a packer test by the United States Geological Survey (U.S.G.S.). It was believed that a packer test would yield additional information as to the source of contamination of the St. Peter Sandstone aquifer.

The well was deepened 25 feet to 515 feet below the land surface in April, 1982. In June, 1982 the U.S.G.S. performed a series of packer tests. The potentiometric surface of ground water in the St. Peter Sandstone aquifer was determined at that time to be 343' below the land surface. These tests proved that the movement of ground water in this location is downward from the Galena-Platteville into the St. Peter Sandstone aquifer, since the water level in the well was observed to be over 70' above the potentiometric surface of the ground water in the St. Peter Sandstone. The tests did not identify any one particular path of contamination.

In the opinion of the Geological and Natural History Survey, there are essentially two possible means to contaminate the ground water in the vicinity of this well. The first is along the annular space at the new well. The second is along some fracture or other drill hole that penetrated the St. Peter near the new well (fig. C-1). A break in the casing may also be a source of communication between the two aquifers.

The annular space around the new well would be a path of communication allowing movement of water down from the Galena-Platteville aquifer into the St. Peter Sandstone aquifer under any of a combination of the following conditions: a grout-to-casing or a grout-to-rock formation separation due to shrinkage; an incomplete grout job due to the filling of some fracture in the Galena-Platteville with grout thus leaving some portion of the annular space below the water table unsealed; or, a mixture of excess water with grout during the grouting procedure producing a poor-quality grout which is permeable.

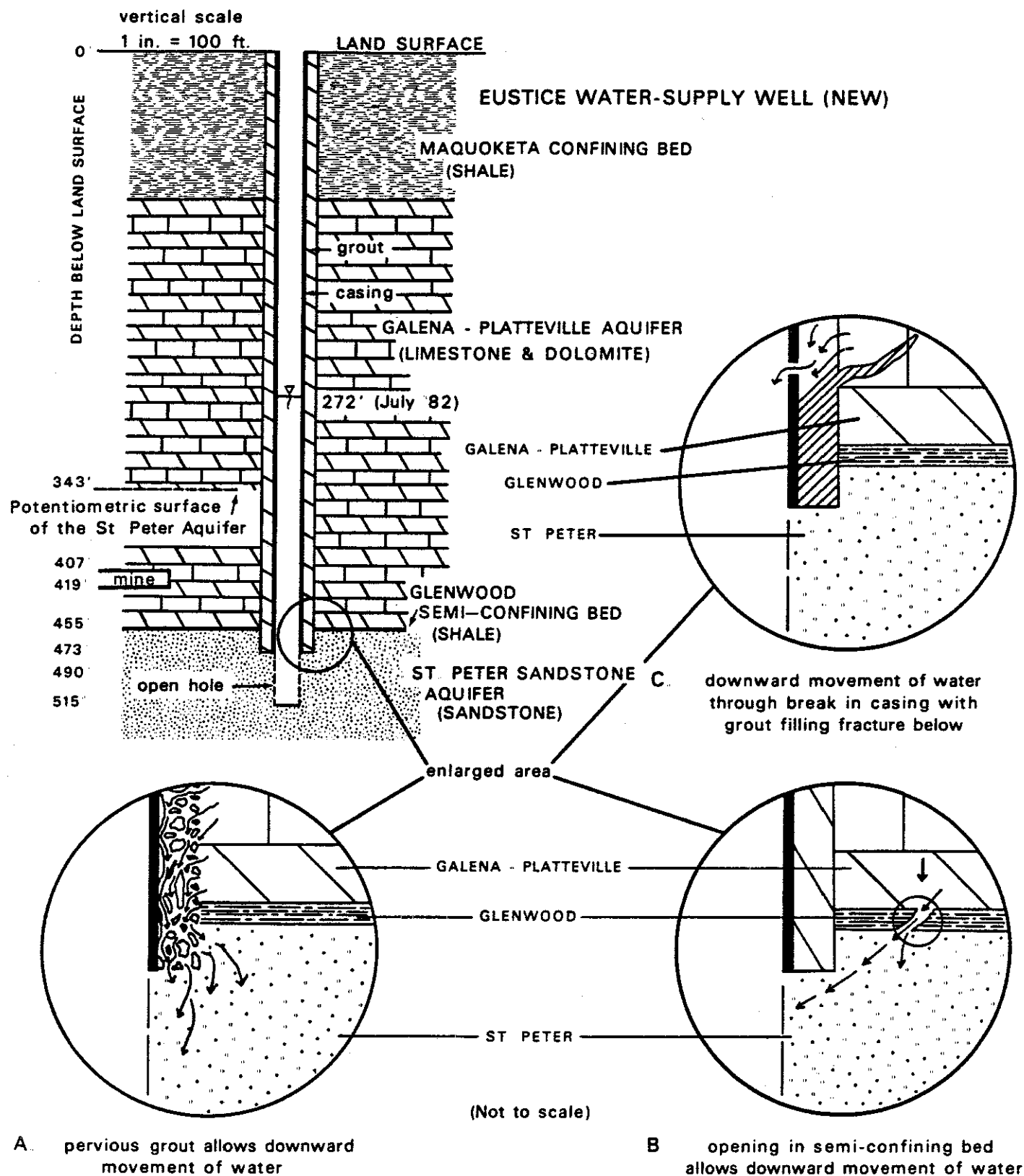


Figure C-1. Diagrammatic representation of well construction of new Eustice/McCord private water-supply well illustrating possible causes of continuing adverse water quality despite new well construction.

The old well (#6) on the Eustice property penetrated approximately 40 feet into the St. Peter Sandstone to a total well depth of 495 feet, according to the well driller. Since there is a net downward movement of ground water resulting from the recovery of the water table towards its pre-mining level, this well was a source of contamination for about one year (based on inferred water levels) before it was abandoned by plugging it with cement upon drilling of the new well (#24). Other drill holes may still be open to the St. Peter Sandstone and may be acting as a means of communication between the two aquifers. The possibility that a fracture extends through the Glenwood semi-confining bed is also possible. Furthermore, it is possible that the Glenwood is not present at some location near the well or, even if present, the Glenwood may allow some flow through it.

The Sedgwick Well (#17)

The Sedgwick residence is in SW $\frac{1}{4}$ SW $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 22, T. 1 N., R. 2 E. The well was originally sampled as an area sampling source. It was chosen because of its location within the cone of depression as defined by the mine-permit application and its construction allowed water from both the Galena-Platteville and St. Peter Sandstone aquifers to be mixed. The authors were interested in this well, because the residents had not complained about adverse water quality and it was believed that the well could reasonably have been expected to be sulfate-impacted. The sulfate levels in the water increased from 41 mg/l in October of 1980, prior to the Survey's study, to 2700 mg/l in October of 1981, the first sampling completed by the Survey on this well. The well became impacted with high sulfate water some time over the 12-month interval between sampling. During the time that the increase in sulfates was detected, the water level in the main shaft rose about 30 ft from 855 ft above sea level to 885 ft above sea level. Water in the vicinity of this well may have encountered a zone which contains oxidized iron sulfides. This well remains in use as of December 1982.

The Wesley Coulthard (#29) and Mrs. Ervin March (#25) Wells

The Wesley Coulthard and Mrs. March wells are of special interest due to the particular history of water-quality impact. Both wells experienced delayed impact of high sulfate waters. Both wells were sampled upon request of a third party.

Mrs. March's well (#25) is located in the NW $\frac{1}{4}$ NE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 26, T. 1 N., R. 2 E. The first Geological and Natural History Survey sample was taken on March 12, 1982. The analysis indicated a sulfate level of 2100 mg/l. The DNR sampled this well on September 25, 1980 and that analysis showed a sulfate level of 400 mg/l. Further, this well had been sampled by the U.S.G.S. on January 20, 1958 and January 30, 1959 (Holt, undated). These latter analyses indicate sulfate levels of 130 mg/l and 84 mg/l respectively. Subsequent samples from June 1, 1982 and December 22, 1982 for this investigation indicate sulfate levels of 2000 mg/l and 2100 mg/l respectively. Clearly, the

March well (#25) has become impacted by high sulfate waters at some time between September 1980 and March 1982.

The Wesley Coulthard well (#29) is located in NE~~NE~~SE~~SE~~ sec. 29, T. 1 N., R. 2 E. The well was first sampled by the Geological and Natural History Survey on April 23, 1982. The sulfate level indicated by the analysis was 730 mg/l, which was slightly above the 700 mg/l sulfate level used as one parameter to define an impacted well. Subsequent sampling on June 1, 1982 and December 22, 1982 indicated sulfate levels of 720 mg/l and 1100 mg/l respectively. This well is now considered an impacted well.

These two wells are examples of delayed impact with respect to the original complaints investigated in the summer of 1980. The Mrs. March well was identified as an impacted well with the March, 1982 sample. The Wesley Coulthard well was not clearly identified as an impacted well until the December 1982 sampling. In both cases, sampling dates suggest an interval during which the private water supplies in these wells were contaminated with excessive sulfate. Reasons for the delay in sulfate impact for these two wells as compared to the original mid-1980 complaints probably reflects local hydrogeologic conditions and well construction factors.

Unrelated Samples

During the contract period, three water samples were taken which can be considered as unrelated to the shutdown of either the Shullsburg or the Bear-hole mines. Two of these samples were taken from households that are on the northwest edge of the town of Lead Mine (#26, #30). These two households are about four miles from the nearest mine working. The other sample (unnumbered) was taken from a household in section 13, T. 1 N., R. 1 E. which is about 2.4 miles from the nearest mine working. Results of the sampling of this latter water-supply well are not included in Appendix A.

The analysis from these samples did not indicate water problems associated with the mine shutdown. None of the parameters measured showed unusually high concentrations.