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Hydrologic Assessment of the Upper Dorr Run Watershed, Hocking County, Ohio, 1998

Water-Resources Investigations Report 99-4137



COVER: Pond formed by beaver dam at sampling sit A3 (looking east from
sampling site A7), Upper Dorr Run Watershed, Hocking County, Ohio.

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

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By Ralph J. Haefner

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Columbus, Ohio
1999

U.S. DEPARTMENT OF THE INTERIOR
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Columbus, Ohio
1999

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PLATE

[Plate is in pocket]

1. Map showing Upper Dorr Run Watershed and locations of sampling sites, Hocking County, Ohio

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CONVERSION FACTORS AND VERTICAL DATUM

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
yard (yd)	0.9144	meter
mile (mi)	1.609	kilometer
Area		
acre	4,047	square meter
square inch (in ²)	6.452	square centimeter
square foot (ft ²)	0.09290	square meter
square mile (mi ²)	2.590	square kilometer
Volume		
gallon (gal)	3.785	liter
gallon (gal)	0.003785	cubic meter

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

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

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

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

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

Altitude, as used in this report, refers to distance above or below sea level.

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

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (μg/L).

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by Ralph J. Haefner

ABSTRACT

The Upper Dorr Run Watershed in Hocking County, Ohio, has been mined several times for coal and clay since 1913 and is a significant source of acid mine drainage to the Hocking River. To assess the surface-water hydrology of the site, a topographic map showing the location of springs and other hydrologic features of interest was prepared using aerial photography and field surveying and mapping techniques. Discharge and water-quality measurements at six springs and one stream site were made during field investigations in June 1998.

Discharge and water quality observed at a downstream weir on Upper Dorr Run represents the combined discharge from springs plus ground-water inflow. Discharges from springs to surface water were generally small (less than 0.3 cubic foot per second), but one spring constituted 56 percent of the total discharge measured at the downstream weir. The total flow at an intermediate measurement site was less than the combined discharge of the upgradient springs because of evaporation, transpiration, and ground-water flow beneath the stream channel. The total flow at the weir was greater than the combined discharge of all springs, primarily because two potential sources of water were not included in field measurements.

The water quality in Upper Dorr Run is strongly affected by acid mine drainage as indicated by pH less than 4, elevated acidity, and elevated concentrations of dissolved sulfate and dissolved iron. Concentrations of chemical con-

stituents in the water were lower at the downstream weir than at the source springs because of residence times in ponds and chemical interactions between the water and the atmosphere. Acidity loads during the sampling period were significantly higher from the Lower Kittanning (No. 5) coal (272 kilograms per day) than from the Upper Kittanning (No. 6) coal (17.7 kilograms per day). Comparison of data obtained in 1998 to data obtained in 1982 showed that quality of water of selected sampling sites had not changed appreciably in 16 years.

INTRODUCTION

The Upper Dorr Run Watershed has been mined for coal and clay several times by surface and underground methods, starting about 1913 and continuing through the early 1970's. The mines were partly reclaimed after deep mining ceased, but not until the late 1970's and again in the mid-1980's. Reclamation involved surface-mining activities only, and it included regrading of spoil, planting of trees, and surface application of papermill sludge; as of 1998, however, surface-water quality indicated that the watershed was still a significant source of acid mine drainage to the Hocking River. Reclamation efforts did not attempt to reduce storage or flow of water in underground mine voids.

In 1998, the U.S. Geological Survey (USGS), in cooperation with the U.S. Department of Agriculture, Forest Service, investigated the Upper Dorr Run Watershed to identify the sources of water contributing to acid mine drainage. The site was visited on three different occasions during the spring and summer of 1998; activities during the visits included field map-

ping, measurement of discharge, and measurement of selected water-quality characteristics. In addition, aerial photographs were obtained to provide hard copy and digital representations of the watershed.

Hydrogeologic setting

Upper Dorr Run is in Hocking County, Ohio, within the Wayne National Forest (fig. 1). The Upper Dorr Run Watershed (hereafter called the study area) is bounded by hills with relief up to 200 ft. Surface water that flows from the study area flows into Dorr Run, which drains southeastward into the Hocking River. The rocks underlying the watershed are Pennsylvanian-age sandstones, shales, coals, and clay (fig. 2). The reported dips of the rocks generally do not exceed 1 degree to the southeast (Lichty and others, 1982). Mining records available from the Ohio Department of Natural Resources (ODNR) document six separate mining operations that extracted the Lower Kittanning (No. 5) clay and the Middle Kittanning (No. 6) coal.

The primary source of water to the study area is rainfall. The watershed is bounded by topographic divides that also serve as surface-water divides. The removal of clay and coal at the study area may have altered the ground-water recharge area to include an area that differs from the surface-water drainage area. In undisturbed hydrogeologic settings, the shallow potentiometric surface commonly mimics the surface topography; however, subsurface mining creates mine voids that may serve as conduits for ground-water flow.

Mining and reclamation history

The study area is characterized by eroded highwalls, berms composed of spoil, and surface-water impoundments that formed behind the berms. Springs¹ are perched on top of clay units and may be found at the base of highwalls and on the floor of the valley. Streambeds and some of the ponds contain red- and orange-stained precipitates of iron, manganese, and aluminum hydroxides.

The mining history of the study area is documented in ODNR mining records and is summarized

¹Springs are usually defined as naturally flowing sources of water emanating from the ground; however, for the purposes of this report, the term "spring" is used for any source of water emanating from the ground, whether natural or manmade.

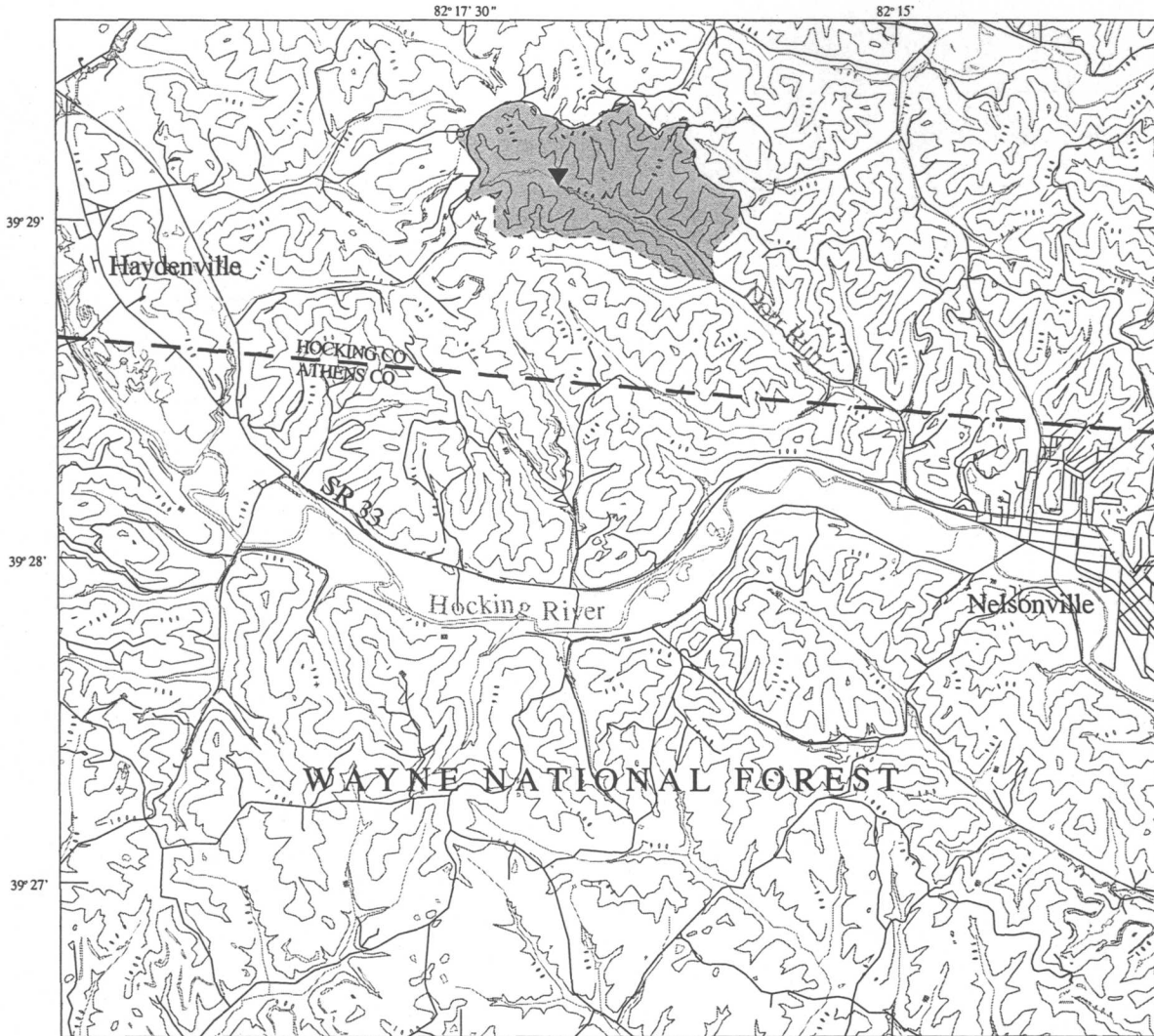
by Lichty and others (1982). The study area was previously owned by the Weltzheimer family; thus, much of the work completed at this study area refers to the Weltzheimer mine site. At least six episodes of mining, beginning as early as 1913, have been documented. The Lower Kittanning (No. 5) clay was extracted by means of room-and-pillar methods, whereas the overlying Middle Kittanning (No. 6) coal was removed by underground- and surface-mining methods. Mining of coal and clay resulted in the formation of spoil piles and highwalls along the No. 6 outcrop. Mining operations ceased in 1972 because of surface-water-quality problems and forfeiture of the mining and reclamation bond by the owner because he refused to reclaim the site and treat the surface water.

The pre-reclamation geologic and hydrologic setting are described in detail by Lichty and others (1982), who provided site-reconnaissance data and proposed various reclamation techniques to seal the abandoned underground mine voids. Surface reclamation was done, however, without regard to the recommendations of Lichty and others (1982). Most mine openings were not sealed but were covered with spoil during regrading.

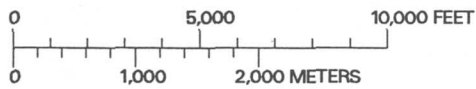
Some of the major findings of Lichty and others (1982) that are important to this study are the following:

- Springs from the Middle Kittanning (No. 6) produce water with much lower volume and of better quality than those from the Lower Kittanning (No. 5).
- The integrity of old mine openings was seriously degraded as a result of collapse.
- Much of the overlying sandstone collapsed into voids left after the removal of the Lower Kittanning (No. 5) clay.

The first reclamation of the study area began in 1977 and included regrading of spoil in areas south and west of the current study area. Additional reclamation work in the mid-1980's included regrading of spoil, planting of trees, and addition of papermill sludge. Spoil piles were shaped during reclamation into berms that served to reduce streamflow and sediment transport by blocking surface drainage. These berms also force surface drainage from upstream valleys to collect in ponds. Thus, the only paths by which surface runoff can leave the site are evapotranspiration or flow through spoil. Spoil at the base of the valleys was graded to form a relatively flat valley floor. Because surface-mining techniques typically involve the



Base map from digital line graph files of
 U.S. Geological Survey, Union Furnace 1961,
 revised 1995; Nelsonville 1961, photorevised 1985;
 Polyconic projection



EXPLANATION






-  Extent of watershed
-  Topography
(contour interval 100 ft)
-  Road
-  Stream
-  Weir

Figure 1. Location of the Upper Dorr Run Watershed, Hocking County, Ohio.

Formation or member	Thickness (feet)	Comments
Lower Freeport Sandstone	25-30	Highwall created during mining of No. 6 Coal
Unnamed shale	0-3	
Middle Kittanning Coal (No. 6)	3-6	Surface and underground mined
Middle Kittanning Clay (No. 6)	1	Extent of mining unknown
Sandstone	3-4	Few outcrops along valley floor
Shale	20	
Lower Kittanning Coal (No. 5)	3	Extent of mining unknown
Lower Kittanning Clay (No. 5)	11	Underground mining techniques only

Figure 2. Generalized stratigraphic section of Pennsylvanian-age rocks at the Upper Dorr Run Watershed, Hocking County, Ohio. (Modified from Hull, 1990, and Lichty and others, 1982.)

removal of fertile layers of soil, organic matter was added to the spoil to support vegetative growth. The added organic matter was provided by papermill sludge (commercially known as BYPRO), which was trucked in from the Mead paper plant in Chillicothe, Ohio. The papermill sludge was applied at a rate of 225 tons per acre over 64 acres.

Purpose and scope

This report describes the sources of water to the Upper Dorr Run Watershed and provides insight to the sources of acidic drainage to the watershed. The study was limited in scope to the investigation of the flow and quality of surface water within Upper Dorr Run. The topography of the watershed and flowpaths of surface water were defined by aerial mapping. Discharge and water quality were measured at seven sites to aid in describing the sources of acid mine drainage in the watershed.

Acknowledgments

The author acknowledges the contribution of the U.S. Department of Agriculture, Forest Service, for technical support throughout this study. Marsha Wikle and Pamela Stachler (both employees of the Forest Service) were instrumental in the planning and implementation of this study. Ms. Stachler provided assistance in selecting sampling sites, sampling-site preparation, and field work. Appreciation is also expressed to Matthew Whitehead of the USGS, who helped measure discharge and collect other data at the study site.

STUDY METHODS

Several methods were used to characterize the surface water in the watershed, including aerial photography, digital mapping, field mapping, measurement of discharge, and measurement of selected water-quality characteristics.

Aerial photography and mapping

Aerial photography and digital mapping were done in spring 1998 to obtain an accurate and current depiction of the land surface and to determine the location of hydrologic features at the study area. A 2-ft digital contour-interval map of Upper Dorr Run was developed using aerial photogrammetric techniques. The watershed was photographed on April 24, 1998. The aerial photos depicted a total of seven aerial-map control points required to produce the contour map. The USGS did land surveys to establish the vertical- and horizontal-control data of the seven aerial-map control points and provided the aerial-map control-point data for development of the digital mapping. The mapping data were checked for quality control and assessed by the USGS as conforming to American Society for Photogrammetry and Remote Sensing (1990) standards. The USGS was provided with DXF (Drawing Interchange File) computer files of the final data. The USGS imported these data into a geographic information system (ARC/INFO) for production of a final map.

After the aerial photography and digital map were obtained, field mapping of hydrologic features was done through site visits and surveying of sampling and measurement points. Elevation and locational measurements of springs, seeps, surface-water bodies, and selected sampling sites were made by means of an electronic theodolite (Sokkia Set II B).

Measurement of discharge

Discharge measurements were made once at each of six springs and two stream sites on June 25-26, 1998. Because no measurable rainfall was recorded seven days prior to the discharge measurements, most discharge was believed to be from base flow (surface runoff was negligible). The diffuse nature of flow from all of the springs made discharge measurement difficult or impossible by use of conventional techniques. Instead, the flow of water from each of these springs was diverted by use of sandbags or soil dikes into a 4- or 6-in.-diameter PVC pipe or into a dug channel. Discharge at five springs was measured using the volumetric technique (measuring the amount of time it took to fill a 5-gal bucket). Discharge measurements at one spring and two stream sites were made with a depth-width-integrated technique and a Price Pigmy current meter. Duplicate or triplicate measurements were made

to ensure reproducibility and accuracy of all measurements and to verify stable hydrologic conditions during sampling. Discharge measurements given in this report are mean values for all measurements taken. All measurements were estimated to be within 5 percent of the actual discharge.

Measurement of water-quality characteristics

Water-quality characteristics were measured in the field at seven spring and stream sites at the same time as discharge measurements. Temperature, pH, specific conductance, reduction-oxidation (redox) potential, and dissolved oxygen concentrations were measured with a Hydrolab H2O five-parameter meter according to standard USGS methods (Wilde and Radtke, 1998). Total acidity determinations were made on sample aliquots that were filtered with an inline filter (0.45- μm pore size). Acidity was measured by hot peroxide titration with 1.6 N sodium hydroxide; thus, the values presented in this report represent total acidity from the hydronium ion (H_3O^+) and potential hydrolysis of hydrated metals. Measurements of concentrations of dissolved sulfate, ferrous iron, and total iron (ferrous plus ferric iron) were made with a Hach spectrophotometer on filtered samples. Reported accuracy levels of spectrophotometric methods are $\pm 10 \mu\text{g/L}$ for ferrous and total iron and $\pm 2.2 \text{ mg/L}$ for sulfate.

Additional measurements of pH, temperature, specific conductance, redox potential, and dissolved oxygen concentrations were made at ponds throughout the study area. Water from the ponds was not analyzed for dissolved ferrous and total iron, sulfate, and acidity, however, because of funding and time limitations.

HYDROLOGIC ASSESSMENT

The results of this study are intended to assist the U.S. Department of Agriculture, Forest Service, in the understanding of likely flowpaths of surface water and sources of acidic drainage at the Upper Dorr Run Watershed. A map of current landforms and features of hydrologic interest is presented, along with a description of the quality of water in springs, streams, and ponds.

Map and current landforms

A detailed topographic map of the study area is shown on plate 1. Also shown on this map are the location of spoil berms, highwalls, and all sampling and measurement sites. Examination of landforms on this map and landforms in unmined areas shows that the topography of the study area has been significantly altered by surface and underground mining and reclamation. Highwalls 30 to 40 ft tall have been left along sandstone outcrops above the No. 6 coal. Although most of the spoil has been regraded to form a flat valley floor, small spoil piles remain throughout the watershed. Spoil berms limit surface runoff and hold water in ponds, thus limiting the departure of water from the site to evapotranspiration or to ground-water flow through spoil materials. The probable extent of spoil fill within the valleys was inferred by breaks in topography and field mapping. Springs along outcrops and on the valley floor may indicate the locations of abandoned mine openings.

In Lichty and others (1982, p. 7), the topography of the watershed is shown before the last reclamation. Several differences are evident between the landscape shown in Lichty and others (1982) and that shown on plate 1 in this report. First, the extent and distribution of ponds has been changed by reclamation activities and construction of beaver dams. Specifically, ponds at sampling sites A10 and A11 had not yet formed or were significantly smaller in 1982. The ponds at sampling sites A1, A3, A9, and A13 are the result of blockage of water by limestone dams and (or) beaver dams. Second, mine entrances shown in Lichty and others (1982) have been obscured by eroding highwalls and (or) regrading of spoil. Third, many of the springs shown in Lichty and others (1982) were not found during the 1998 field investigations. It is possible that different flow conditions existed during the measurements made by Lichty and others (1982) as compared to the measurements made in this study; however, the measurements made by Lichty and others (1982) were made during June and August, and flows from springs that were found in 1982 and in 1998 were similar to each other. The disappearance of some springs indicates that the distribution of flow has changed since 1982 because of seasonal effects, changes in ground-water levels at the study area, or additional collapse of mine voids.

Discharge relations

Six springs were identified during field mapping of the Upper Dorr Run Watershed in 1998. Discharge from all measured sites is given in table 1. Some of these springs feed into small streams or ponds and combine to form the discharge measured at the weir at the downstream end of the watershed. (See, for example, springs at sites S1, S2, and S3.) Other springs, such as those at sampling sites S4, S5, and S6, produce water that flows over rock outcrops and infiltrates into spoil on the valley floor.

Discharge from springs was generally small (less than $0.3 \text{ ft}^3/\text{s}$). The flow from S1 contributed approximately 56 percent of the outflow from the watershed measured at the downstream weir. The combined outflow from the No. 6 coal for the 1998 measurement period was $0.034 \text{ ft}^3/\text{s}$, whereas the combined outflow from the No. 5 coal was $0.341 \text{ ft}^3/\text{s}$. This order-of-magnitude difference confirms one of the conclusions of Lichty and others (1982); namely, that the springs emanating from the No. 6 coal produce much lower volume than springs from the No. 5 coal.

A water balance was computed to compare combined discharge from selected springs to measurements made at downstream sites (table 2). If all gains or losses of water from the springs to the outflow at the weir were accounted for, then the sum of the discharges from springs should equal the discharge measured at the weir (within a 5-percent measurement error). To supplement discharge measurements at springs and the weir, an additional discharge measurement was made upstream from sampling site S3 (plate 1). The water-balance calculations in table 2 show a loss of $0.019 \text{ ft}^3/\text{s}$ between the combined discharge of springs S1, S2, S4, S5, and S6 and the measurement site above S3. Possible explanations of the loss of water include evaporation or transpiration of water from ponds, loss of surface-water flow to ground water, and (or) measurement error (± 5 percent). Discharge from S4 and S5 was observed to infiltrate into spoil filling the valley floor. This water may flow within the spoil beneath the streambed or within bedrock and bypass the measurement site above S3.

Summation of the discharge from S3 and the measurement site above S3 yields a total of $0.356 \text{ ft}^3/\text{s}$. This sum differs from the flow measured at the downstream weir by $0.068 \text{ ft}^3/\text{s}$ (an increase of 16 percent). The most likely cause of this discrepancy is that two additional sources of water were located between the

Table 1. Discharge data for springs and a surface-water site at the Upper Dorr Run Watershed, Hocking County, Ohio
[ft; feet; ft³/s, cubic foot per second]

USGS site identifier	Local identifier ¹	Altitude (ft)	Date	Time	Mean discharge (ft ³ /s)	Measurement method ²	Stratigraphic interval of origin
Spring sites							
392916082170800	S1	836.27	06/25/98	1200	0.238	P	No. 5 Coal
392918082170500	S2	832.23	06/25/98	1530	.052	V	No. 5 Coal
392916082170500	S3	819.86	06/25/98	1330	.051	V	No. 5 Coal
392920082170900	S4	881.02	06/26/98	0900	.003	V	No. 6 Coal
392918082172200	S5	887.60	06/26/98	1000	.020	V	No. 6 Coal
392914082171100	S6	884.07	06/26/98	1100	.011	V	No. 6 Coal
Stream site							
392911082165700	Weir	795.25	06/25/98	1100	.424	P	--

¹Site locations are shown on plate 1.

²Measurement methods: P, Price Pigmy current meter; V, volumetric technique

spring at S3 and the weir that were not measured during field activities. First, a seep was observed along the northern edge of the beaver pond at measurement site A1. The diffuse nature of flow at this site made discharge measurements and collection of water samples impossible. Second, and probably more significant, an additional tributary just upstream from the weir was not included in the water-balance calculation. This tributary was located by examination of the aerial photographs after the field mapping and reconnaissance, and the project team was unaware of this site at the time discharge measurements were made. An additional possible cause of this gain of water is that the stream gained water from ground-water inflow through the streambed.

Water quality

Water-quality data from springs and the downstream weir are listed in table 3. These data show that water discharging from springs is acid mine drainage, as evident from a pH less than 4 and elevated concentrations of acidity, dissolved sulfate, and dissolved iron.

A wide range of temperatures was found among spring sites. This was primarily due to the proximity of the sampling site to the location where water first made contact with the atmosphere. Greater distance of the sampling site from the source of the spring resulted in longer contact time with the warm atmosphere, which was about 30°C (85°F) during the two-day sampling effort. This effect can be seen by comparing water temperature from any of the springs to the water temperature at the downstream weir. The representative temperature of spring water during the June 1998 sampling event was likely 10-12°C (50-54°F).

As noted previously, pH values for all spring sites and the downstream weir were less than 4.0. Oxidation and dissolution of pyritic mine spoil releases protons (in the form of the hydronium ion), resulting in low pH and elevated concentrations of iron, sulfate, and dissolved solids. Although concentrations of other elements, such as aluminum and manganese, were not measured during this study, the low pH of water that results from pyrite oxidation also contributes to elevated concentrations of these elements. Specific conductance (an approximate indicator of dissolved solids concentration) of water from all spring sites and the downstream weir was greater than 1,000 µS/cm.

Table 2. Water balance for springs and surface water at the Upper Dorr Run Watershed, Hocking County, Ohio

[ft³/s, cubic foot per second]

Site	Discharge (ft ³ /s)
1. S1	0.238
2. S2	.052
3. S4	.003
4. S5	.020
5. S6	.011
6. TOTAL (1+2+3+4+5)	0.324
7. Measurement site above S3	0.305
8. Difference (7-6)	-0.019
9. S3	0.051
10. TOTAL (7+9)	0.356
11. Weir	0.424
12. Difference (11-10)	0.068

Concentrations of dissolved oxygen were difficult to interpret because any agitation of the water or increased contact time with the atmosphere has the potential to increase the concentration. Minimum dissolved oxygen concentrations of 0.6 and 0.7 mg/L, measured at spring sites S2 and S1, respectively, are probably representative of the spring water at the study area. In contrast, dissolved oxygen values and temperature at sites S3, S4, and S6 were greater than 5.0 mg/L and 15°C, respectively, indicating agitation and (or) extended contact time with the atmosphere.

The reduction-oxidation (redox) potential of water is an indicator of reducing or oxidizing conditions, but it must be interpreted with caution because of assumptions regarding the equilibrium state of water and the presence of a dominant redox couple (Stumm

and Morgan, 1981). Because many different redox couples contribute to the redox value measured in a water sample, an assumption was made that, for these measurements, the dominant redox couple was ferrous and ferric iron (Fe²⁺ and Fe³⁺, respectively; Nordstrom and others, 1979). If water is in an equilibrium state, higher redox values should correspond to greater concentrations of oxidized (ferric) iron.

Redox values did not vary significantly between sampling sites. The most oxidizing water was from springs at sampling sites S4 and S5, whereas the least oxidizing water was from the spring at S1. Accordingly, water from S4 and S5 have relatively high concentrations of ferric iron, whereas water from S1 is dominated by ferrous iron.

Total acidity concentrations (as mg/L of CaCO₃) of water sampled at spring sites ranged from 158 to 508 mg/L. At four of the six springs, acidity concentrations were less than 200 mg/L; however, the spring at S1, which also had the greatest discharge, had an acidity concentration of 388 mg/L.

Sulfate concentrations ranged from 350 mg/L in water from S6 to 1,300 mg/L at spring S1. Total iron concentrations varied over 2 orders of magnitude, from a minimum of 2.9 mg/L at sampling site S2 to 120 mg/L at S1. These values are within the range of concentrations of sulfate and iron from other watersheds in Ohio that are affected by acid mine drainage (Engelke and others, 1981).

As inferred from elevation and location, springs at sampling sites S4, S5, and S6 emanate from the No. 6 coal, whereas springs at sampling sites S1, S2, and S3 emanate from the No. 5 coal or underclay. Although originating from the same coal formation, water from spring S4 is distinctly different from that observed at S5 and S6. Spring S4 had the lowest pH (2.6) and the highest specific conductance and acidity of any site sampled during this study. There may be many reasons that the water quality at this site differs from that at S5 and S6, including a difference in drainage area (which might include differences in geology and abundance or morphology of sulfide minerals), different mining techniques, and a longer residence time of water within the flow system. Site S4, however, is of minor importance with respect to the overall quality of water that leaves the study area through the downstream weir because discharge at site S4 was the smallest of any site measured (0.003 ft³/s). As a percentage of total discharge measured at the downstream weir, spring S4 represents less than 1 percent of the flow from the watershed.

Table 3. Water-quality data for samples collected at the Upper Dorr Run Watershed, Hocking County, Ohio, June 25-26, 1998
 [deg. C, degrees Celsius; $\mu\text{S}/\text{cm}$, microsiemens per centimeter; mg/L milligrams per liter; mv, millivolts]

USGS site identifier	Local identifier	Date	Time	Temperature (deg. C)	pH	Specific conductance ($\mu\text{S}/\text{cm}$)	Oxygen, dissolved (mg/L)	Reduction oxidation potential (mV)	Acidity (mg/L as CaCO_3)	Sulfate, dissolved (mg/L)	Ferrous iron, dissolved (mg/L)	Total iron, dissolved (mg/L)
Spring sites												
392916082170800	S1	06/25/98	1200	12.9	3.6	1,850	0.7	480	388	1,300	120	120
392918082170500	S2	06/25/98	1530	11.7	3.3	1,320	.6	610	184	730	2.1	2.9
392916082170500	S3	06/25/98	1330	19.6	2.9	1,680	5.7	704	185	700	.7	5.8
392920082170900	S4	06/26/98	0900	20.7	2.6	2,040	8.9	740	508	900	1.8	22
392918082172200	S5	06/26/98	1000	10.4	2.8	1,150	3.1	740	199	480	.4	5.4
392914082171100	S6	06/26/98	1100	15.7	2.9	1,040	12.3	690	158	350	1.6	3.4
Stream site												
392911082165700	Weir	06/25/98	1100	22.3	2.9	1,520	7.8	690	189	710	1.6	11
Pond sites												
	A1	06/26/98	1410	25.4	2.9	1,660	11.4	660	--	--	--	--
	A2	06/26/98	1425	23.2	3.0	1,600	11.7	670	--	--	--	--
	A3	06/26/98	1430	26.5	2.9	1,720	11.9	700	--	--	--	--
	A4	06/26/98	1445	23.9	3.8	550	.8	270	--	--	--	--
	A5	06/26/98	1455	18.0	2.9	980	11.9	660	--	--	--	--
	A6	06/26/98	1500	23.2	2.9	1,900	5.1	670	--	--	--	--
	A7	06/26/98	1505	26.5	2.9	1,910	2.7	640	--	--	--	--
	A8	06/26/98	1510	23.0	4.9	900	2.8	380	--	--	--	--
	A9	06/26/98	1515	27.2	2.9	1,720	9.4	690	--	--	--	--
	A10	06/26/98	1540	21.4	4.1	760	10.2	610	--	--	--	--
	A11	06/26/98	1550	20.3	5.5	850	1.36	190	--	--	--	--
	A13	06/26/98	1610	25.5	3.3	800	4.4	610	--	--	--	--
	A14	06/26/98	1630	20.4	4.3	310	5.7	300	--	--	--	--
	A15	06/26/98	1635	20.5	4.9	180	1.7	280	--	--	--	--

Examination of water quality from springs that flow from the No. 5 coal shows that the sample from S1 had the greatest concentrations of dissolved sulfate and iron of any water sample in the watershed. The water at S1 was also the most reducing (had the lowest redox value) of any water sampled during this study. Because spring water at S1 had the greatest concentration of dissolved iron and sulfate and relatively high total acidity, and because discharge at S1 was greater than that of any of the springs in the watershed, spring S1 is the primary source of acid mine drainage at the study area.

Measurements made at pond sites were intended to give an overview of conditions in slow-moving, relatively stagnant water as compared to streams and springs. These ponds were not observed to have any flowing springs or streams that contributed water to them; therefore, the ponded water probably originated from surface runoff, direct recharge, or ground-water inflow. As discussed previously, contact time with the atmosphere has the potential to affect many of the water-quality characteristics measured during this study. Temperature was much higher in the ponds than in water from the springs and exceeded 20°C in all but one pond. Specific conductance varied over an order of magnitude, from 180 to 1,910 µS/cm. The pH of pond water ranged from 2.9 to 5.5; six pH values at pond sites exceeded the highest pH found among the spring sites and the weir site. Eight specific conductances measured in pond sites were less than the lowest value measured at spring sites and the weir site; most of the low specific conductances were associated with high pH.

FACTORS AFFECTING WATER QUALITY

Loading relations between water quality and discharge are an important consideration towards understanding the sources of contamination in watersheds affected by acid mine drainage. For example, a spring that has a very small discharge might produce water with very high concentrations of dissolved constituents. The net effect of the discharge from this spring may be the same as a spring that has high discharge with very low concentrations of dissolved solids.

Wide ranges of discharge and concentrations of water-quality constituents were found among springs at the Upper Dorr Run Watershed. Load computations were done to compare the relative contributions of dissolved constituents from each spring to the concentra-

tion measured at the downstream weir (table 4). Load was computed by multiplying the concentration of a dissolved constituent measured at a spring or surface-water site by the discharge and applying the appropriate conversion factors. For the purposes of this analysis, loads are daily values given in kilograms (kg/d). For acidity loading at site S1, the following example calculation is provided for clarity:

Acidity concentration: 388 mg/L
 Discharge: 0.238 ft³/s

$$388 \text{ mg/L} \times 0.238 \text{ ft}^3/\text{s} \times 1.0^{-6} \text{ kg/mg} \times 28.32 \text{ L/ft}^3 \times 86,400 \text{ s/d} = 226 \text{ kg/d}$$

For acidity, sulfate, ferrous iron, and total iron, the combined load from all springs was greater than loads calculated for the stream at the downstream weir. In contrast, loads of ferric iron increased between the springs and the weir. Thus, other processes at the Upper Dorr Run Watershed must serve to change the concentrations and (or) redox state of dissolved constituents between the springs and the downstream weir.

The water quality found at the downstream weir is the result of mixing of water from the six springs, contributions from ground water, seepage from ponds, and interaction of water with the atmosphere. Spring S1 is the dominant source of water at the study area and also contributes most of the acidity, dissolved sulfate, and dissolved iron (in the form of Fe²⁺) to the watershed. However, iron concentrations are about an order of magnitude lower at the downstream weir than at spring S1.

As water flows downgradient towards the weir, agitation of the water along the streambed and over beaver dams causes dissolved oxygen concentration and redox potential to increase. Ferrous iron (Fe²⁺) is oxidized to form ferric iron (Fe³⁺), which precipitates to form ferrihydrite (Fe(OH)₃). The solubility of ferrihydrite is limited at low pH. Other multivalent metals, such as aluminum and manganese, behave similarly. An important result of these precipitation reactions is that they release hydronium ions, lowering the pH. This process can be confirmed by comparing the decrease in pH and iron concentrations between S1 and the weir.

The rate at which ferrous iron oxidizes to form ferric iron and precipitate ferrihydrite is slow without the microbiologically enhanced oxidation provided by the bacterium *Thiobacillus ferrooxidans* (Nordstrom,

1985). The iron precipitate was commonly seen in ponds or on the streambed as a red-orange encrustation. Additionally, concentrations of dissolved metals can be decreased by complexation and (or) sorption with organic molecules, inorganic molecules, and clay particles. Although dissolved organic carbon (DOC) was not specifically measured as part of this study, decaying organic matter from vegetation and papermill sludge likely contributes DOC to the ponds and streams in the watershed.

Ponds at the study area also contained suspended colloidal iron precipitates that were observed to be more abundant during sunny, bright conditions. The pond water was almost clear during early morning hours or on cloudy days; yet, in the middle of a sunny day, the water in the ponds was opaque and bright orange. This difference was likely the result of photoreduction and reoxidation of iron (McKnight and others, 1988; Hrcir and McKnight, 1998).

In environments affected by acid mine drainage, sulfate concentrations in water can decrease by processes such as sorption and precipitation of secondary minerals. Sorption occurs on positively charged metal hydroxides, particularly with iron hydroxides

(Webster and others, 1998). Secondary minerals that can precipitate in low-pH settings include jarosite ($KFe_3(SO_4)_2(OH)_6$) and schwertmannite ($Fe_{16}O_{16}OH_{12}(SO_4)_2$). Precipitation of these minerals is similar to precipitation of other metal hydroxides, in that a hydrolysis reaction liberates hydronium ions, causing the pH to decrease.

The reasons behind the decrease in total acidity between some springs and the weir are less clear. By all accounts, total acidity should have increased because of geochemical reactions discussed previously; however, results obtained from the watershed show that acidity concentrations decreased by about 30 percent between S1 and the weir. Even though the previously discussed hydrolysis and precipitation reactions release hydronium ions, they also consume metals, which are components of the total (or "potential") acidity measurement. Thus, the potential contribution from the hydrolysis of metals to acidity may have a significant effect on acidity measurements made at this study area. Additionally, extended residence times in shallow ponds may cause additional geochemical changes augmented by vegetation in a wetland setting (Kleinmann, 1985; Wieder and others, 1982).

Table 4. Load computations for water-quality samples collected at the Upper Dorr Run Watershed, Hocking County, Ohio

[Loads are given in kilograms per day; all samples were analyzed in the field except for ferric iron, which was calculated by difference between total iron and ferrous iron]

Site	Acidity	Sulfate, dissolved	Ferrous Iron, dissolved	Total Iron, dissolved	Ferric Iron, dissolved
S1	226	757	69.9	69.9	0.00
S2	23.4	92.9	.27	.37	.10
S3	23.1	87.4	.09	.72	.64
S4	3.73	6.61	.01	.16	.15
S5	9.74	23.5	.02	.26	.24
S6	<u>4.25</u>	<u>9.42</u>	<u>.04</u>	<u>.09</u>	<u>.05</u>
Sum of springs	290	977	70.3	71.5	1.18
Weir	<u>196</u>	<u>737</u>	<u>1.66</u>	<u>11.4</u>	<u>9.75</u>
Difference	-94.1	-240	-68.7	-60.1	8.57

Water chemistry and flow-system dynamics may change with respect to time, ranging from single-day cycles to seasonal or long-term changes. Daily or seasonal fluctuations may be due to the occurrence and magnitude of recharge events and photoreduction reactions related to the intensity of sunlight. Long-term studies in coal-mining areas in Ohio, such as those documented by Cunningham and Jones (1990) and Eberle and Razem (1985), have shown that significant changes in water quality occur very slowly and may take up to a decade to become evident. The results of this study and those of Lichty and others (1982) are limited by single sampling events that may be representative only of conditions at base flow. Significant seasonal variations in flow and water quality are likely; thus, the following comparisons between data collected during this study and data from Lichty and others is inadequate to draw major conclusions. Comparison of data obtained by Lichty and others (1982) with the results from the present study, however, indicates only minor changes in water quality since 1982 (table 5). (Site identifiers used in this study and Lichty and others (1982) are different; the measurement site at the weir is the same site as Lichty and others' site DR2.) Water-quality values measured at the weir, S4, S5, and S6 (corresponding to Lichty and others' sites DR2, S4 and S5, S1, and GA11-S8, respectively) were similar to those measured in 1982. Acidity and dissolved sulfate have decreased slightly, but there were no changes in pH, specific conductance, or total iron. Water quality

from S1 (which corresponds to Lichty and others' site S6/S7) has changed slightly. pH has increased from 2.8 to 3.6. Acidity and sulfate have decreased, but total iron has increased. The spring at site S1 has the greatest influence on water quality at the site and shows some changes in water quality over time; however, water quality at the weir (Lichty and others' site DR2) remains unchanged. Thus, if seasonal conditions were similar between the two measurement dates, reclamation and natural attenuation had little influence on the water quality of the watershed after 16 years.

SUMMARY AND CONCLUSIONS

The Upper Dorr Run Watershed in Hocking County, Ohio, has been mined several times since 1913. Reclamation efforts during the 1970's and 1980's focused on planting of trees, regrading of spoil, and application of papermill sludge; however, the study area is still a significant source of acid mine drainage. An investigation by the USGS in 1998 showed that discharges from springs to surface-water bodies were generally small (less than 0.3 ft³/s) and that one spring constituted more than half of the total discharge measured at a downstream weir. The total flow at an intermediate measurement site was 6 percent less than the combined discharge of five of the six springs, probably because of evaporation and transpiration from ponds, ground-water flow beneath the stream channel, and

Table 5. Comparison of water-quality data from prereclamation (Lichty and others, 1982) and this study
[μ S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L milligrams per liter; --, no data]

Results from this study						Results from Lichty and others (1982)					
USGS site Identifier	pH	Specific-conductance (μ S/cm)	Acidity (mg/L)	Total iron, dissolved (mg/L)	Sulfate, dissolved (mg/L)	Lichty and others (1982) site Identifier	pH	Specific-conductance (μ S/cm)	Acidity (mg/L)	Total iron, dissolved (mg/L)	Sulfate, dissolved (mg/L)
WEIR	2.9	1,520	189	11	710	DR2	3.1	1,650	--	14.5	1,250
S1	3.6	1,850	388	120	1,300	S6/S7	2.8	1,800 2,200	650 560	10.0 18.7	1,910
S4	2.6	2,040	508	22	900	S4	2.7	2,100	650	10.0	--
S5	2.8	1,150	199	5.4	480	S5		1,950	390		
S6	2.9	1,040	158	3.4	350	S1	2.8	2,200	580	10.0	--
						GA11-S8	--	900	140	9.0	--

measurement error. The total flow at the downstream weir was greater than the combined discharge of all springs by 16 percent, primarily because two potential sources of water were excluded during field measurements.

The water quality at the study area is dominated by the effects of acid mine drainage. Concentrations of acidity, sulfate, and iron are elevated at all sites in the watershed but are significantly lower at the downstream weir because of geochemical interactions between the water and the atmosphere. Comparison of water-quality data obtained in 1998 and in 1982 show that water at selected sampling sites has not changed appreciably.

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