

Water-Quality Data at Selected Sites in the Mississippi-Valley-Type Zn-Pb Ore District of Upper Silesia, Poland, 1995-97

By Laurie Wirt¹, Jacek Motyka², David Leach¹, Maria Sass-Gustkiewicz², Marek Szuwarzynski³, Zbigniew Adamczyk⁴, Paul Briggs¹, and Al Meiers¹

U.S. Geological Survey

Open-File Report 01-283

This report is preliminary and has not been reviewed for conformity with the U.S. Geological Survey editorial standards. Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

¹ U.S. Geological Survey, Denver, Colorado, United States

² University of Mining and Metallurgy, Cracow, Poland

³ Trzebionka Mine, Trzebinia, Poland

⁴ Boleslaw Mine and Metallurgy Unit, Poland

CONTENTS

Abstract.....	4
Introduction.....	4
Purpose and Scope.....	6
Description of Study Area.....	8
Regional Differences in aquifer characteristics.....	9
Quaternary.....	10
Jurassic.....	10
Triassic.....	11
Paleozoic.....	11
Methods of Study.....	11
Field Measurements.....	12
Sample Preparation.....	12
Analytical Techniques.....	13
Quality Assurance.....	14
Field Equipment Blanks.....	15
Sequential Replicates.....	15
Standard Reference Samples.....	15
Ion Balances.....	17
Acknowledgements.....	17
References.....	18

FIGURES

1. Map showing location of the Upper Silesia Ore District, Poland.
2. Map showing regional geology, important mines (active and inactive), and undeveloped MVT deposits in the Upper Silesian Ore District, Poland.
3. Stratigraphic column of post-Paleozoic rocks in the Upper Silesia Ore District, Poland.
4. Generalized hydrogeologic cross-section of the Upper Silesia Ore District, Poland.

TABLES

1. Explanation of database terms and abbreviations used to code sampling environment
2. Explanation of descriptive terms and abbreviations used to code samples with respect to geographic, geologic, and hydrologic parameters
3. Water-quality sampling sites at selected mines, waste or tailings ponds, springs, wells, and streams showing descriptive sampling codes
4. Analytical detection limits reported by laboratories used in the study
5. Chemical analyses of field equipment blanks collected during the study
6. Comparison of chemical analyses of environmental samples and sequential replicates analyzed by ICP-MS
7. Statistical comparison of chemical analyses of standard reference waters
8. Water-quality data tables for dissolved constituents by ICP-AES (USGS)
9. Water-quality data tables for dissolved constituents by ICP-MS (USGS)
10. Water-quality data tables for total constituents by ICP-MS (ActLabs)

CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
inch (in)	2.54	centimeter (cm)
mile (mi)	1.609	kilometer (km)
liter (L)	0.2641	gallons (US)
foot (ft)	0.3048	meter (m)

Water-Quality Data at Selected Sites in the Mississippi-Valley-Type Zn-Pb Ore District of Upper Silesia, Poland, 1995-97

By Laurie Wirt¹, Jacek Motyka², David Leach¹, Maria Sass-Gustkiewicz², Marek Szuwarzynski³, Zbigniew Adamczyk⁴, Paul Briggs¹, and Al. Meiers¹

Abstract

The water chemistry of aquifers and streams in the Upper Silesia Ore District, Poland are affected by their proximity to zinc, lead, and silver ores and by ongoing mining activities that date back to the 11th century. This report presents hydrologic and water-quality data collected as part of a collaborative research effort of the U.S. Geological Survey and the University of Mining and Metallurgy in Cracow, Poland to study Mississippi-Valley-Type lead-zinc deposits. MVT deposits in the Upper Silesia Ore District (Fig. 1) were selected for detailed study because the Polish mining industry allowed access to collect samples from underground mines and mine-land property. Water-quality samples were collected from streams, springs, wells, underground mine seeps and drains; and mine-tailings ponds. Data include field measurements of specific conductance, pH, water temperature, and dissolved oxygen and laboratory analyses of major and minor inorganic constituents and selected trace-element constituents.

INTRODUCTION

The Upper Silesia Ore District is one of the world's great Mississippi Valley Type lead-zinc (MVT Zn-Pb) ore districts. The first recorded mining began in the 11th century and originally exploited silver and lead. Zinc became the major commodity during the middle of 19th century. Although the total production of ore in the district is not precisely known, it is estimated that 500 million metric tons of

ore were produced in 800 years of continuous mining. Mining activity started in several ore fields around the towns of Bytom, Tarnowskie Gory, Siewierz, Chrzanow and Olkusz (Fig. 2 - mine locations). Active mining in the district is presently restricted to two mines in the Olkusz area (Olkusz and Pomorzany mines) and one in the Chrzanow areas (Trzebionka mine). Mines in the Bytom area are depleted and have been closed. Presently there are five deposits prepared for production and eight in the resource assessment stage in the Zawiercie area (Przenioslo et al., 1999). Remaining ore reserves are estimated to be about 200 Mt of sulfide ore with average ore grades of 3.8% Zn and 1.6% Pb. In addition, there are about 57 million metric tons of uneconomic oxidized ore with an average grade of 5.6 % Zn and 1.4% Pb. Four active mines produce annually 5 million metric tons of ore (about 200 thousand tons of metallic zinc and 57 thousand tons of metallic lead (Przenioslo, 1997). Mining is an integral component of the Polish economy, and mineral production is expected to continue as Poland increasingly participates in expanding European and global economies. Future development of new ore deposits in the district, however, hinges in part on local concerns about degradation of the environment (Mayer and others, 1996).

Recently, there has been much interest by the Polish and European governments in mitigating the environmental effects of mining in this intensively industrial region. In addition, the United States government has an interest in regulation and remediation of zinc and lead mines on its own soil. Effective and cost-efficient management of mineral resources requires knowledge about the degree of contamination from anthropogenic activities and the water-rock interactions near ore bodies that affect water chemistry. In 1995, a collaborative research effort was established between the U.S. Geological Survey (USGS) and the University of Mining and Metallurgy (UMM) in Cracow, Poland to provide data that can be used to develop a global geo-environmental model for MVT deposits. The geology and ore mineral assemblage of the Upper Silesia zinc-lead district are similar to other MVT ore districts in the world (Leach and Viets, 1996) and

these deposits were some of the most readily accessible for scientists to study. A specific goal of the research effort is to describe the geological and hydrological characteristics of the ore district. This information will be used to improve understanding of the processes that control the occurrence and transport of contaminants and to identify mining sites that have the most adverse affect on water quality and the environment.

Purpose and Scope

The purpose of this report is to present water-quality data and methods of data collection at selected sampling sites in the Upper Silesia Ore District in southern Poland. Data were collected from October 1995 to December 1997 as part of a collaborative effort between the USGS and UMM scientists. Ground-water and surface-water samples were collected primarily in the Olkusz and Trzebinia areas of the ore district, but also near Czatkowice where no ore mining has occurred. Ground-water samples consisted of 26 springs, 17 wells, and more than 130 water samples from underground mine seeps discharging from the major Quaternary, Jurassic, Triassic, Permian, and Carboniferous aquifers. Surface-water samples were collected from 28 stream reaches and four waste or tailings ponds.

Each sample was coded with respect to selected hydrologic and geologic parameters. Important hydrologic parameters (Table 1) included the type of flow, whether water had been in contact with ore or anthropogenic contamination, and the saturation state of the aquifer (for ground-water samples). Important geological parameters (Table 2) included the age and lithology of the rock unit, and a determination of the aquifer represented by the water sample. Interpretations were required to determine whether a mine seep was derived from a “Jurassic” versus “Triassic” aquifer (or was a composite of both) and whether or not it had been in contact with ore. Coding assignments were determined on the basis of the professional judgement of co-author Jacek Motyka, having more than 30 years of professional experience as a mining-

engineering hydrologist in the Upper Silesia ore district. The objective of the coding was to manage the data and allow that various environmental properties of the water samples could be readily compared with the dissolved chemistry of selected constituents.

Most of the mine seep samples were collected from active underground outflows drips or seeps. Some were collected from mine pumps or drains used to facilitate mine dewatering. In at least four cases, the water sampled was a composite of multiple mine seeps. In this report, the term “background” is used to refer to water that has not been in contact with ore (which includes both mined ore or tailings as well as undisturbed ore). At least 119 of the mine-seep samples are thought to have been in contact with ore and 12 samples are thought to represent background conditions in the aquifer. Background samples were also collected from 17 stream reaches, 24 springs, and 4 wells that represent background conditions in Quaternary, Jurassic, Triassic, Permian, and Carboniferous aquifers; for a total of 54 background samples. Additional water samples were collected that were contaminated by anthropogenic activities unrelated to mining but present in the study area, including fly ash (2 samples), industrial waste (6 samples), and river water contaminated by sewage (5 samples). Thus, out of a database of 195 water samples, at least 28 percent represent non-mining background conditions and 72 percent have been in contact with ore. Not all samples that have been in contact with ore, however, would be defined as having been contaminated by human activities. Many samples that have been in contact with ore are also coded as representative of background conditions in the aquifer.

Description of the Study Area

The Upper Silesia Ore District is in a northwestern trending belt in southern Poland about 30 to 80 kilometers northwest of Cracow. The region surrounds the towns of Chrzanów, Olkusz, Bytom, Tarnowskie Góry, and Zawiercie, which were largely developed as mining and industrial centers following the two World Wars (Fig. 2). Topography consists of relatively low-lying ridges and gentle valleys that have been smoothed by glacial activity. Surficial drainage is from east to west to the Biata Przemsza and its major tributaries, the Jaworznik and Sztola rivers.

Ore deposition in the Upper Silesia region occurs in the Devonian, Carboniferous, Triassic and Jurassic carbonates with the bulk of the ores hosted by Triassic and Devonian rocks. At present, only the Triassic ores have been mined. Ores hosted in Devonian rocks are also of economic-grade but still have not been developed. The minor mineralization in Jurassic limestones is closely connected with Lower Tertiary faults and fractures.

Water-quality sampling was focused on two areas of active mining; one is the Olkusz area that contains the Olkusz and Pomorzany mines and the other is the Trzebinia (or Chrzanow) area that contains the Trzebionka mine. The ore deposits in the Olkusz and Trzebinia areas have nearly identical contents of sphalerite and galena (about 4.6 to 4.7 % sphalerite and 1.7 to 1.9 % galena). However, mines in the two areas contain distinctly different amounts of iron sulfides and concentrations of trace elements contained in the mineral assemblages. Ores in the Olkusz area contain about 6 to 15 % iron sulfides (pyrite plus marcasite) whereas the ores in the Trzebinia area contain less than 2 % iron sulfides (Leach and others, 1996).

Regional differences in the occurrence of the aquifers

The main source of ground water is recharge from surface runoff. Precipitation averages about 70 cm/yr and is greater along Jurassic ridges in the northeast part of the study area, which are 400 to 500 meters above sea level. Historically, ground-water discharge is to springs and to the Biala Przemsza river basin in the Olkusz region and to the Przemsza and Rudawa river basins in the Trzebinia (or Chrzanow) region. At the present time, however, the largest source of ground-water withdrawals is from mining. Mine water is generally discharged to streams although it is sometimes used for water supply to local towns and villages. Two broad hydro-geological regions can be distinguished: Olkusz region (Olkusz, Pomorzany and Boleslaw mines) and Chrzanow region (Trzebionka mine). Ground-water conditions may be confined or unconfined, however, mine dewatering has caused large cones of depression near each of the mining districts, and a regional lowering of the water table. All of the adjoining aquifer units tend to be interconnected to some degree, except where noted.

The schematic hydro-geological cross section in [Fig. 3](#) shows typical hydrologic relationships. The Triassic aquifer in Olkusz region is more exposed near the surface, resulting in direct recharge of local precipitation. Shallow recharge of ground water results in relatively more oxidized conditions than in the Trzebinia region, where the Triassic aquifer is confined and hydrologic conditions are slightly reducing. Aquifers in Olkusz region tend to be better interconnected than in Trzebinia region.

In the region between Trzebinia and Olkusz, the Triassic aquifer is absent, and Upper Carboniferous sandstone forms an unconfined aquifer of good quality that is used for public supply. In Trzebinia area, however, the sandstone overlies Triassic carbonates and forms a second confined aquifer. Not all water from the Paleozoic rocks is of good quality. Economic deposits of coal in the Upper Carboniferous sandstone and clay in the Trzebinia region contain Na-Cl type brines.

Before the advent of mine dewatering, the regional flow direction was predominantly from east to west. At present, pumping from mining and water supply wells has resulted in a deep cone of depression approximately 400 km² that extends around the Boleslaw, Olkusz, and Pomorzany mines. The combined rate of pumping for these three mines in the year 2000 was about 6 m³/s. The potentiometric surface of the Triassic aquifer has been lowered by as much as 40 meters (m) in the Boleslaw Mine, 130 m in the Pomorzany Mine, 80 m in the Olkusz Mine and about 200 m in the Trzebionka Mine.

The principal aquifers are described (see Fig. 4) from youngest to oldest below:

Quaternary. The unconsolidated Quaternary aquifer is composed of fluvial-glacial sand and gravel. The Quaternary deposits fill buried paleo-valleys and modern valleys overlying the Jurassic and Triassic aquifers. Deposits are generally shallow and surficial, ranging from 10 to 70 m in thickness. Because of the relative homogeneity of the alluvium, the hydraulic conductivity, as measured by pumping tests, is about 10⁻⁴ m/s (Motyka and others, 1994).

Jurassic. Jurassic limestone forms an unconfined aquifer in the east and northeastern part of the study area and ranges up to 100 m in thickness. Primary permeability occurs along connected fissures and solution features. The Jurassic rocks unconformably overlie the Triassic and Paleozoic rocks. Water levels have been lowered in the Jurassic aquifer in the Olkusz and Pomorzany regions. Hydraulic conductivity, as measured by pumping tests, ranges from 10⁻⁶ to 10⁻⁴ m/s (Motyka and others, 1994).

Triassic. Middle and Lower Triassic dolomite and limestone units comprise the most extensive aquifer in the study area. The water-bearing dolomite also contains the main ore deposits. A relatively impermeable clay unit, or marl,

commonly separates the base of the Jurassic from the Triassic aquifer. Water exchanges between the two rock formations in a few local areas where the marl is absent and the Triassic and Jurassic units are in direct contact. The aquifer ranges from 0 to 150 meters in thickness and unconformably overlies both semi-permeable Permian conglomerates and permeable Devonian and Lower Carboniferous carbonates. Porosity occurs, in order of importance a) as primary porosity within the matrix (2-11%), b) along fissures and fractures (<0.2%), and c) in caverns (<0.5%) (Motyka, 1998). Hydraulic conductivity ranges from 10^{-6} to 10^{-3} m/s, as measured by pumping tests (Motyka and others, 1994).

Paleozoic. The Triassic aquifer is underlain in most areas by a Paleozoic unconformity that lies from 100 to 300 m beneath the land surface. Paleozoic strata include a semi-permeable Permian conglomerate, which forms a semi-permeable confining unit, and Lower Carboniferous and Devonian carbonates, which form a deeper confined aquifer with water of good quality under artesian pressure. Hydraulic conductivity for the Paleozoic aquifer ranges from 10^{-6} to 10^{-5} m/s (Motyka and others, 1994).

METHODS OF STUDY

Water quality samples were collected from October 1995 to December 1997 by a team of USGS and UMM scientists. The sites are listed in [Table 3](#). Various individuals collected the samples at different times of the year. Because the majority of the samples were collected from several underground mines and also two caves, latitude and longitude coordinates could not be determined accurately. More detailed information regarding the rock mineral assemblages of sampling locations is discussed in Leach and others (1996) and Sass-Gustkiewicz and others (1982).

Field measurements

USGS and Polish scientists collected water samples using appropriate USGS standard protocols (see Wilde and Radtke, 1998). Field parameters measured at the time of sample collection included specific conductivity, pH, dissolved oxygen, and water temperature. Field meters were calibrated in the morning on the day of sample collection. The pH meters were calibrated with pH-4 and pH-7 buffers or pH-7 and pH-10 buffers to bracket the range of pH values measured in the field. Specific conductance meters were also calibrated with standards that bracketed the range of values expected at the sampling sites. Dissolved oxygen was measured using a visual colorimetric test kit. The test kit utilizes indigo carmine, which reacts with oxygen to form a blue product. The color intensity of the sample is then visually compared with that of known standards to determine the concentration of dissolved oxygen.

Sample preparation

All sampling equipment and bottles in contact with the water sample were cleaned with deionized water and pre-rinsed with sample water. Surface-water samples were collected using the dip method. Mine seeps were collected from underground passages by allowing the dripping water to flow into the bottle or by dipping into a mine pool. Wells were pumped continuously until field parameters had stabilized prior to collecting the sample. Raw or unfiltered aliquots were collected for analysis of total concentrations of major and trace elements. Both raw and filtered aliquots were acidified to a pH of less than 2 using nitric acid. Filtering of samples was generally performed onsite, using a disposable 0.45- μ M cellulose nitrate capsule filter and a 100-ml plastic syringe. The syringe was rinsed three times and then filled with raw sample water. A capsule filter was then attached to the end of the syringe and the sample was forced through the filter into the sample bottle. Sample containers were rinsed with filtered sample water before being filled. This process was repeated until the required volume of filtered sample was obtained. In a few cases, mining employees collected mine-seep samples that were later processed by project scientists at the office.

Analytical Techniques

Analytical techniques used for water-quality analyses and their corresponding analytical detection limits are listed in [Table 4](#). Major anions; including bicarbonate, chloride, and sulfate; were determined at a university laboratory in Cracow. The analysis was generally conducted within 24 hours of sample collection. Bicarbonate was determined from filtered samples using 0.05 molar HCl acid by Gran titration. Sulfate was determined by the capillary electrophoresis system (CES type 270 A-HT) produced by “Applied Biosystems.” Chloride was determined by the method of Mohr using 0.01 or 0.1 molar AgNO₃, nitrate, and sulfate. Samples destined for analysis of major cations and trace metals were shipped by air to the United States.

Dissolved major, minor, and trace-metal concentrations were analyzed by two methods in a USGS laboratory in Denver, Colorado. Filtered acidified samples were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) as described by Briggs and Fey (1996) and by (ICP-MS) as described by Lamothe and others (1999). A subset of acidified, unfiltered water samples was sent to a commercial laboratory, Activation Laboratories, Ltd. (Actlabs) in Wheat Ridge, Colorado. The Actlabs samples were analyzed by ICP-MS using a quadrupole mass spectrometer. Analytical detection limits for the three laboratories are in [Table 4](#).

QUALITY ASSURANCE

Quality-assurance procedures used during the study include daily calibration of water-quality meters, cleaning of sampling equipment and rinsing of sample bottles, and collection of field blanks and replicate samples.

The quality of the laboratory analyses was assessed through the analysis of laboratory blanks, sample replicates, and USGS standard reference water samples (Long and Farrar, 1995; anonymous author, 1996) and calculated ion

balances. A total of 5 deionized water sample blanks and 15 replicate split samples were submitted for laboratory analysis (Table 5). In addition, 34 standard reference samples were blindly submitted to the three laboratories. The analytical accuracy, precision, and detection limits for selected chemical constituents from each laboratory are given in Tables 6-8.

Field Equipment Blanks

A field-equipment blank is a sample prepared using deionized water that is passed through all the sampling equipment. This type of sample is used to check for potential contamination of environmental samples during sampling collection, processing, handling, and analysis. Analytical results for the field equipment blanks collected during the study period are listed in Table 5. The measured concentrations for most constituents were generally at or below the detection limits of the analytical methods. Several samples did have detectable concentrations of constituents, although with a few exceptions, most concentrations were less than twice the analytical detection limit.

Sequential Replicates

Sequential replicate samples are collected to estimate the variability in the sample data. In the sequential replicate, a replicate sample is collected as close in time as possible to the environmental sample. Each sample is processed through all the normal steps of a regular water-quality sample (Spahr and Boulger, 1997). For each step of sample processing, the environmental sample is processed before the replicate sample.

A total of 14 sequential replicates were collected during the study period. Comparison of analytical results between environmental samples and sequential replicates for major, minor, and selected trace-element constituents are listed in Table 6. For the samples analyzed by the USGS ICP-AES and ICP-MS methods, the majority of the differences between the environmental and the sequential replicates are within ± 10 percent. For samples analyzed by Actlabs

by ICP-MS, the majority of differences between the environmental and the sequential replicates are also less than ± 10 percent.

In many instances, however, dissolved samples analyzed by USGS were considerably different (by more than ± 10 percent) than total samples analyzed by Actlabs. Although one might expect the value of total analyses to be greater than or equal to that of the dissolved analyses for the same water sample, this was not always the case. For example, total Ca and Ti values tended to be lower than their respective dissolved values; whereas total Cr, Se, Tl, and Th values tended to be substantially higher than their respective dissolved values. In the case of Mg, Pb, Mn, and Rb, however, some dissolved values were higher and some were lower than the total values.

Standard Reference Samples

The precision and accuracy of ICP-MS laboratory analyses was evaluated by analyzing a total of 67 standard reference samples (Table 7). Two standard reference waters (T-135 and T-137) were chosen to represent waters having different concentrations of analytes that were similar to the range of what might be encountered in the study area. The U.S. Geological Survey Branch of Quality systems (Anonymous, 1996; Long and Farrar, 1995) has determined the most probable values for the standard reference water samples by distributing the reference waters to a group of participating water-quality laboratories.

The precision of reference samples analyzed by USGS ICP-MS was generally within 20 percent of the most probable value for a given constituent. Notable exceptions include As and Ba; and low-range Cu, Fe, and Mn. The precision of reference samples analyzed by USGS ICP-AES was also generally within ± 20 percent of the most probable value for a given constituent, with the exception of Al and Mo and low-range Cd, Cu, Mn, and Mo. Analysis of Ba and Fe by ICP-AES was generally more accurate than by ICP-MS. Accuracy exceeded ± 20 percent for Al, As, Ba, Mo, and low-level Fe, Mn, and Pb.

The precision of reference samples analyzed by Actlabs ICP-MS exceeded 20 percent for more elements in comparison to the precision of USGS samples. Precision greater than ± 20 percent was observed for Mg, Al, Fe, Mo, Ni, U, and Zn; and low-range Cu and Mn. In addition, accuracy exceeded ± 20 percent for Mn, Mo, Fe, and Zn.

The statistical analysis of variance for the two laboratories using ICP-MS exceeded 20 percent error for As, Ba, Fe, Mo, Sb, Ti, V, and Zn for analysis of reference sample T-137. In the case of reference sample T-135, the ± 20 percent error threshold was exceeded for Al, Ba, Mn, Fe, Mo, Pb, Sb, Ti, U, V, and Zn. The large differences in the values of various constituents by USGS ICP-MS and Actlabs ICP-MS may be partly attributed to filtering of the USGS samples. The best analytical agreement between the two laboratories using ICP-MS was for the elements Ca, Mg, Na, Cd, Co, Cu, Li, Ni, Se, and Sr.

Ion Balances

Analytical results for the three laboratories (USGS ICP-AES, USGS ICP-MS, and Actlabs ICP-MS) are given in [Tables 8-10](#). In addition to analysis of quality-assurance samples, the accuracy of major cations (Ca, Mg, Na) and anions (SO_4 , HCO_3 , Cl) was evaluated by calculating the ion balance, which is a calculated value in the last column of each table. In general, many of the ion balances exceeded five percent of the difference between the sum of major cations and the sum of major anions. Hem (1992) notes that the test of the ion balance does not accurately evaluate the accuracy of water when large concentrations of a few constituents are present, as is the case for the water from mine seeps that has been in contact with mineralized ores. In addition, many of the ground-water samples were probably in the process of equilibrating with the atmosphere at the time the sample was collected. Samples were not analyzed immediately, but were shipped overseas, potentially undergoing large elevation and pressure differences before being delivered to the Denver

laboratories. Thus, more weight was placed on the precision and accuracy of the standard reference samples than on the ion balance.

Acknowledgements

Many aspects of this study would not have been possible without the cooperation of mining officials at the Olkusz, Pomorzany, and Trzebieonka mines. The authors are indebted for the contributions of several USGS employees; J.G. Viets, and A.L. Meier provided chemical analysis and statistical expertise; any data-handling errors, however, are attributed solely to the authors. James Paschal managed the organization and design of the database; and Geoff Plumlee provided helpful discussion. Project management in Poland was coordinated by Maria Sass-Gustkiewicz.

REFERENCES

- Anonymous author, 1996, Report on the U.S. Geological Survey's evaluation program for standard reference samples distributed in October 1995: T-137 (trace constituents), M-136 (major constituents), N-47 (nutrients), N-48 (nutrients), P-25 (low ionic strength constituents), Hg-21 (mercury) and SED-5 (bed material): U.S. Geological Survey Open-File Report 96-138, p. 106.
- Briggs, P.H., and Fey, D.L., 1996, Twenty-four elements in natural and acid mine waters by inductively coupled plasma-atomic emission spectrometry: in B. F. Arbogast, ed., Analytical methods manual for the Mineral Resource Surveys Program, U.S. Geological Survey Open-File Report 96-525, p. 95-101.
- Hem, J. D., 1992, Study and interpretation of the chemical characteristics of natural water: U.S. Geological Survey Water-Supply Paper 2254, 263 p.
- Lamothe, P.J., Meier, A. L., and Wilson, Stephen, 1999, The determination of forty-four elements in aqueous samples by inductively coupled plasma-mass spectrometry: U.S. Geological Survey Open-File Report 99-151, 14 p.
- Leach, D. L. and Viets, J. G., 1992, Comparison of the Cracow-Silesian Mississippi Valley-type district, southern Poland, with Mississippi Valley-type deposits in North America: U.S. Geol. Survey Open-File Report OF/92-704, 72 pp.

- Leach, D.L., Viets, J.B., Kozłowski, A., and Kibitlewski, S., 1996, Geology, geochemistry, and genesis of the Silesia-Cracow zinc-lead district, southern Poland, *in* Sangster, D.F, ed., Carbonate-hosted Lead-Zinc Deposits: Society of Economic Geologists Special Publication 4, p. 144-170.
- Long, H.K., and Farrar, J.W., 1995, Report on the U.S. Geological Survey's evaluation program for standard reference samples distributed May 1995—T-135 (trace constituents), M-134 (major constituents), N-45 (nutrients), N-46 (nutrients), P-24 (low ionic strength), Hg-20 (mercury) and SED-5 (bed material): U.S. Geological Survey Open-File Report 95-395, 135 p.
- Mayer, W., Motyka J., Sass-Gustkiewicz, M., Szuwarzynski, M. Leach, D. L., Plumlee, G., and Viets, J.G., Environmental geochemistry of the Upper Silesia Zinc-Lead District: Society of Economic Geology Newsletter, 26, p. 8-9.
- Motyka, J., 1998, A conceptual model of hydraulic networks in carbonate rocks illustrated by examples from Poland: *Hydrogeology Journal*, 6, p. 469-482.
- Motyka, J., Witczak, S., and Zuber, A., 1994, Migration of lignosulfonates in a karstic-fractured-porous aquifer: History and prognosis for a Zn-Pb mine, Pomorzany, southern Poland: *Environmental Geology*, 24, p. 144-149.
- Przeniosło, 1997, Mineral and groundwater resources statistics in Poland: Polish Geological Institute, Warsaw, Poland 352 p. (*in Polish*)
- Sass-Gustkiewicz, M., M. Dzulynski, S., and Ridge, J.D., 1982, The emplacement of Zn-Pb sulfide ores in the Upper Silesian District—a contribution to the understanding of Mississippi Valley-type deposits: *Economic Geology*, v. 77, p 392-412.
- Spahr, N.E., and Boulger, R.W., 1997, Interim results of quality-control sampling of surface water for the Upper Colorado River National Water-Quality Assessment Study Unit, water years 1995-96: U.S. Geological Survey Water Resources Investigations Report 90-140, 71 p.
- Wilde, F.D., and Radtke, D.B., 1998, National field manual for collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6.