6. Fate and Transport: Behavior of Contaminants Moving across Media Boundaries

METAL BEHAVIOR DURING SURFACE-GROUNDWATER INTERACTION, SILVER BOW CREEK, MONTANA
Benner, Shawn G. (University of Montana, Missoula); E.W. Smart; J.N. Moore
Environmental Science & Technology, Vol 29 No 7, p 1789-1795, Jul 1995

The fate of heavy metals in a stream-groundwater system tainted with mine-related metals was monitored in Silver Bow Creek, MT. Geochemical processes representative of surface-acidic groundwater interaction were defined with a unique in situ method of sampling the solid phase chemistry and by water chemistry analyses. The composition of the 1 m-thick hyporheic zone in bed sediment was explained by a mixing ratio of 96:4 surface water to polluted groundwater. This zone may serve as a sink for metals and metal loading to bed sediment may be significant.

GEOCHEMICAL PROCESSES IN GROUND WATER RESULTING FROM SURFACE MINING OF COAL AT THE BIG SKY AND WEST DECKER MINE AREAS, SOUTHEASTERN MONTANA
Clark, D.W.
USGS Water-Resources Investigations Report 95-4097, 80 p, 1995

A potential hydrologic effect of surface mining of coal in southeastern Montana is a change in the quality of ground water. Dissolved-solids concen- trations in water in spoils aquifers generally are larger than concentrations in water in the coal aquifers they replaced; however, laboratory experiments have indicated that concentrations can decrease if ground water flows from coal-mine spoils to coal. This study was conducted to determine if decreases in concentrations occur onsite and, if so, which geochemical processes caused the decreases. Solid-phase core samples of spoils, unmined over- burden, and coal, and ground-water samples were collected from 16 observation wells at two mine areas. In the Big Sky Mine area, changes in ground-water chemistry along a flow path from an upgradient coal aquifer to a spoils aquifer probably were a result of dedolomitization. Dissolved-solids concentrations were unchanged as water flowed from a spoils aquifer to a downgradient coal aquifer. In the West Decker Mine area, dissolved-solids concentrations apparently decreased from about 4,100 to 2,100 milligrams per liter as water moved along an inferred flow path from a spoils aquifer to a downgradient coal aquifer. Geochemical models were used to analyze changes in water chemistry on the basis of results of solid-phase and aqueous geochemical characteristics. Geochemical processes postulated to result in the apparent decrease in dissolved-solids concentrations along this inferred flow path include bacterial reduction of sulfate, reverse cation exchange within the coal, and precipitation of carbonate and iron-sulfide minerals.

REACTIVE UPTAKE OF TRACE METALS IN THE HYPORHEIC ZONE OF A MINING-CONTAMINATED STREAM, PINAL CREEK, ARIZONA
Fuller, C.C.; J.W. Harvey, U.S. Geological Survey, Menlo Park, CA
Environmental Science & Technology, Vol 34 No 7, p 1150-1155, 1 Apr 2000

Significant uptake of dissolved metals occurred by interaction of groundwater and surface water with hyporheic-zone sediments during transport in Pinal Creek, AZ. The extent of trace metal uptake was calculated by mass balance measurements made directly within the hyporheic zone. A conservative solute tracer injected into the stream was used to quantify hydrologic exchange with the stream and groundwater.

Fractional reactive uptake of dissolved metals entering the hyporheic zone was determined at 29 sites and averaged 52 +/- 25, 27 +/- 19, and 36 +/- 24% for Co, Ni, and Zn, compared with Mn uptake of 22 +/- 19%. First-order rate constants (lambda(h)) of metal uptake in the hyporheic zone were determined at seven sites using the exchange rate of water derived from tracer arrival in the streambed. Reaction-time constants (1/lambda(h)) averaged 0.41, 0.84, and 0.38 h for Co, Ni, and Zn, respectively, and 1.3 h for Mn. In laboratory experiments with streambed sediments, metal uptake increased with preexisting Mn oxide concentration, supporting our interpretation that Mn oxides in the hyporheic zone enhance trace metal uptake. Reach-scale mass-balance calculations that include groundwater metal inputs indicated that decreases in metal loads ranged from 12 to 68% over the 7-km perennial reach depending on the metal. The decreases in metal loads are attributed to uptake of trace metals by Mn oxides in the hyporheic zone that is enhanced because of ongoing Mn oxide formation. Analysis of dissolved-metal streambed profiles and conservative solute tracers provide a valuable tool for quantifying metal uptake or release in the hyporheic zone of contaminated streams.

WATER RESOURCES MANAGEMENT IN RIVER BASINS: AN INTERDISCIPLINARY AND TRANSBOUNDARY CHALLENGE

Grunewald U., Lehrstuhl fur Hydrologie, Brandenburgische Tech. Univ. Cottbus, Cottbus, Germany

Hydrologie und Wasserbewirtschaftung, Vol 43 No 6, p 292-301, 1999

In the present discussion about the new European water guideline in Germany, we should continue the already existing experiences and methods of water resources management in river basins. According to the special planning or managing tasks several detailed methods are available. It is necessary to connect these methods with the different instruments of the regional and environmental planning. The strong connection of modern model techniques of water quantity management with equivalent methods of water quality management considering the interactions of groundwater and surface water systems is presented. This is illustrated for the three transboundary catchments of the rivers Spree, Schwarze Elster and Neisse in East-Germany, which are influenced by lignite mining.

HYDROGEOLOGY AND GEOCHEMISTRY OF ACID MINE DRAINAGE IN GROUND WATER IN THE VICINITY OF PENN MINE AND CAMANCHE RESERVOIR, CALAVERAS COUNTY, CALIFORNIA: SECOND YEAR SUMMARY, 1992-93

Hamlin, S.N.; C.N. Alpers

USGS WaterResources Investigations Report 96-4257, 44 pp, 1996

Acid drainage from the Penn Mine in Calaveras County, California, has produced a plume of contamination in ground water between Mine Run Dam and Camanche Reservoir. Historically, contaminated surface runoff from the mine flowed directly into the Mokelumne River; after the construction of Camanche Dam in 1963, the surface runoff flowed into Camanche Reservoir. Interaction of surface water with sulfide bearing waste rock and mill tailings has produced acidic surface water with pH values between 2.3 and 2.8 and high concentrations of sulfate and metals including aluminum, cadmium, copper, iron, and zinc. Diversions and unlined impoundments were constructed in 1978 to prevent or reduce surface runoff from the mine. Some of the impounded
mine drainage infiltrates to the ground water through fractures in bedrock and flows toward Camanche Reservoir. The lowermost impoundment was treated with lime for several months during 1993 to raise pH and to immobilize contaminants, but the impoundment has since been allowed to resume its untreated condition. This report summarizes the findings from the first 2 years of study by the U.S. Geological Survey of contaminated ground water at the Penn Mine. The distribution and flow of ground water at the

Penn Mine is controlled by geologic features and hydraulic properties. Geologic controls include fractures in bedrock, faults, and the contact between the principal rock types in the area. Most flow occurs through fractures in a metavolcanic unit along its contact with an underlying metasedimentary (slate) unit. The median hydraulic conductivity is about 10 times higher in the
metavolcanic unit (0.1 foot per day) than in the slate unit (about 0.01 foot per day). Most flow occurs in the fractured metavolcanic rocks; hydraulic conductivity in this unit is as high as 50 feet per day. The general hydraulic gradient in ground water in the area between Mine Run Dam and Camanche Reservoir is westward toward Camanche Reservoir. Field data show a close relation between water quality in Mine Run Reservoir and water quality in downgradient wells in an area covered by slag. Specific conductance at all wells increased between April and December 1992. During the same period, some wells showed a decrease in pH and an increase in dissolved metals concentration, reflecting a higher proportion of acid drainage in the ground water. Heavy stable isotopes of hydrogen and oxygen are enriched in the impounded surface water, as well as in the ground water downgradient from the impoundments. These stable isotope data indicate that the partially evaporated water in the impoundments is the most likely source of contamination to the fractured rock aquifer in the slag area between Mine Run Dam and Camanche Reservoir. Water from the underground mine workings is chemically distinct from ground water in the slag area. Exsolved gas compositions in water from the flooded mine workings indicate somewhat reducing conditions. Ratios of dissolved concentrations of zinc to copper and of zinc to cadmium are anomalously high in the underground mine water in comparison with such ratios for ground water in the slag area. These data suggest preferential scavenging of copper and cadmium, relative to zinc, by hydrogen sulfide produced by sulfate reduction in the mine workings. Variations in stable isotopes of sulfur and oxygen in dissolved sulfate are consistent with this interpretation. Discharge toward Camanche Reservoir within the acidic groundwater plume at the base of Mine Run Dam is estimated to be about 40 cubic feet (300 gallons) per day, using an average hydraulic gradient of 0.07 and a geometric mean value for hydraulic conductivity of 0.1 foot per day based on a total of five measurements from three wells in this immediate area. The actual rates of groundwater discharge in the contaminant plume vary with plume width, hydraulic gradient, and hydraulic properties of the fracturedrock aquifer. The hydraulic gradient varies with seasonal changes in recharge and in the water level of Camanche Reservoir. For the flow rate of 40 cubic feet per day, the corresponding loadings of dissolved metals flowing toward Camanche
Reservoir were estimated to be 17 grams of copper per day, 250 grams of zinc per day, and 2.7 grams of cadmium per day.

EFFECT OF ENHANCED MANGANESE OXIDATION IN THE HYPORHEIC ZONE ON BASIN-SCALE GEOCHEMICAL MASS BALANCE
Harvey, J.W.; C.C. Fuller
Water Resources Research, Vol 34 No 4, p 623-636, 1998

INTERACTIONS BETWEEN SHALLOW GROUND WATER AND SURFACE WATER THAT AFFECT METAL TRANSPORT IN PINAL CREEK, ARIZONA
Harvey, J.W.; C.C. Fuller; B.J. Wagner
U.S. Geological Survey Toxic Substances Hydrology Program: Proceedings of the Technical Meeting, 20-24 September 1993, Colorado Springs, Colorado
U.S. Geological Survey Water-Resources Investigations Report 94-4015, p 1065-1072, 1996

QUANTIFYING HYDROLOGIC INTERACTIONS BETWEEN STREAMS AND THEIR

SUBSURFACE HYPORHEIC ZONES
Harvey, J.W.; B.J. Wagner
Streams and Ground Waters
Academic Press, 1999

THE EFFECT OF STREAMBED TOPOGRAPHY ON SURFACE-SUBSURFACE WATER EXCHANGE IN MOUNTAIN CATCHMENTS
Harvey, J.W.; K.E. Bencala
Water Resources Research, Vol 29 No 1, p 89-98, 1993

PRELIMINARY INVESTIGATION OF THE EFFECT OF HILLSLOPE HYDROLOGY ON THE MECHANICS OF SOLUTE EXCHANGE BETWEEN STREAMS AND SUBSURFACE GRAVEL ZONES
Harvey, J.W.; K.E. Bencala; G.W. Zellweger
U.S. Geological Survey Toxic Substances Hydrology Program: Proceedings of the Technical Meeting, 11-15 March 1991, Monterey, California
U.S. Geological Survey Water Resources Investigations Report 91-4034, p 413-418, 1991

GEOCHEMICAL PROCESSES IN THE CONTEXT OF HYDROLOGIC TRANSPORT: REACTIONS OF METALS IN ST. KEVIN GULCH, COLORADO
Kimball, B.A.; K.E. Bencala; R.E. Broshears
Proceedings of the American Institute of Hydrology Meeting on Toxic Substances and the Hydrologic Sciences, p 80-94, 1994

HYDROGEOCHEMICAL, ISOTOPIC, AND RARE EARTH ELEMENT EVIDENCE FOR CONTRASTING WATER-ROCK INTERACTIONS AT TWO UNDISTURBED ZN-PB MASSIVE SULPHIDE DEPOSITS, BATHURST MINING CAMP, N.B., CANADA
Leybourne, M.I.; W.D. Goodfellow; D.R. Boyle, Geological Survey of Canada, Ottawa, ON
Journal of Geochemical Exploration, Vol 64 No 1-3, p 237-261, 1999

A detailed hydrochemical study at two undisturbed Ordovician massive sulphide (Zn-Pb) deposits (Restigouche and Halfmile Lake deposits, Bathurst Mining Camp, New Brunswick) was initiated to elucidate the processes controlling the oxidation and dissolution of sulphide minerals, the subsequent dispersion of metals in ground and surface waters, and the precipitation of secondary minerals. Groundwater hydrogeochemical signatures are different for the two deposits. Elements that form sulphide minerals in the deposits correlate positively in surface waters and increase with proximity to the Restigouche deposit, whereas metal contents for Halfmile Lake surface waters are lower, though still typically higher than background levels. Variations in the composition of ground and surface waters draining the two deposits reflect in part differences in the depth and geometry of the massive sulphides and host lithologies. The Halfmile Lake deposit is deeper, more steeply dipping, and overturned compared to the shallower Restigouche deposit. Groundwaters at the Halfmile Lake deposit up to 760 m below surface are low-TDS, Ca-HCO3 to Na-HCO3 waters with oxygen and hydrogen isotopic compositions identical to surface waters. Groundwater REE patterns are flat to LREE-enriched and are similar to host lithologies, unlike the surface waters which are LREE-depleted compared to shale. The Restigouche groundwaters

display heavier oxygen and hydrogen isotopic compositions than local surface waters. Variations in groundwater composition require that the two
deposits have different hydrologies which influence the natural oxidation of the massive sulphides and thus the environmental hydrochemical signature.

EVALUATION OF MINE TAILINGS IMPACT TO THE ENVIRONMENT IN MINERALIZED TERRAINS

Mongrain, R.A.; B.E. Lary; T.O. Looff; E.L.J.Bingham, AGRA Earth and Envtl. Incorporated, Phoenix, AZ

Tailings and Mine Waste '00. Proceedings of the 7th International Conference, January 2000, Fort Collins, January 2000
A.A. Balkema, Netherlands. ISBN: 9058091260. p 489-498, 2000

A tailings impoundment failure resulted in mine tailings and waste rock being deposited into Pinto Creek in Arizona. Resulting impacts were quantified using comprehensive characterization programs. These programs included collection and analysis of data to evaluate the tailings debris, mineralized terrain, effects of historic mining operations, surface water, and alluvial groundwater. Potential effects to water quality, riparian and upland flora and fauna were also evaluated. Geochemical models then integrated data from solid media (Debris, remobilized Debris, residual Debris, Earlier Tailings Residue, and Natural Stream Sediments), and aqueous media (pore water, surface water and alluvial groundwater). Characterization and modeling efforts: 1) identified Potential Constituents of Concern; 2) evaluated geographic distribution of impacts; 3) assessed acid-generation potential of residual Debris and the buffering capacity of alluvial sediments; 4) evaluated adequacy of the Removal Action; 5) assessed impacts and interaction of surface/groundwater quality; and 6) facilitated ecological hazard and human health risk assessments.

AN INTERACTIVE CODE (NETPATH) FOR MODELING NET GEOCHEMICAL REACTIONS ALONG A FLOW PATH-VERSION 2.0

Plummer, L. Niel; Eric C. Prestemon; David L. Parkhurst

U.S. Geological Survey Water-Resources Investigations Report 94-4169, 130 p., 80 references

NETPATH is an interactive Fortran 77 computer program used to interpret net geochemical mass-balance reactions between an initial and final water along a hydrologic flow path. Alternatively, NETPATH computes the mixing proportions of two to five initial waters and net geochemical reactions that can account for the observed composition of a final water. The program utilizes previously defined chemical and isotopic data for waters from a hydrochemical system. For a set of mineral and (or) gas phases hypothesized to be the reactive phases in the system, NETPATH calculates the mass transfers in every possible combination of the selected phases that accounts for the observed changes in the selected chemical and (or) isotopic compositions observed along the flow path. The calculations are of use in interpreting geochemical reactions, mixing proportions, evaporation and (or) dilution of waters, and mineral mass transfer in the chemical and isotopic evolution of natural and environmental waters. Rayleigh distillation calculations are applied to each mass-balance model that satisfies the constraints to predict carbon, sulfur, nitrogen, and strontium isotopic compositions at the end point, including radiocarbon dating. DB is an interactive Fortran 77 computer program used to
enter analytical data into NETPATH, and calculate the distribution of species in aqueous solution. This report describes the types of problems that can be solved, the methods used to solve problems, and the features available in the program to facilitate these solutions. Examples are presented to demonstrate most

of the applications and features of NETPATH. The codes DB and NETPATH can be executed in the UNIX or DOS1 environment. This report replaces U.S. Geological Survey Water-Resources Investigations Report 91-4078, by Plummer and others, which described the original release of NETPATH, version 1.0 (dated December, 1991), and documents revisions and enhancements that are included in version 2.0.

HYDROLOGY AND GEOCHEMISTRY OF A SURFACE COAL MINE IN NORTHWESTERN COLORADO

Williams, R.S. Jr.; G.M. Clark

USGS Water-Resources Investigations Report 92-4187, 61 pp, 1994

The hydrology and geochemistry of a reclaimed coal mine in northwestern Colorado were monitored during water years 1988 and 1989. Some data also were collected in water years 1987 and 1990. This report describes (1) the sources of hydrologic recharge to and discharge from reclaimed spoil, (2) the relative contributions of recharge to the reclaimed spoil aquifer from identified source waters and the rate of water movement from those sources to the reclaimed spoil, and (3) the geochemical reactions that control water quality in reclaimed spoil. The study area was at a dip-slope coal mine encompassing about 7 square miles with land slopes of varying aspect. The area was instrumented and monitored at five sites; two sites had unmined and reclaimed- spoil areas adjacent to each other and three sites were unmined. The mined areas had been reclaimed. Instrumentation at the study sites included 1 climate station, 3 rain gages, 19 soil-water access tubes, 2 lysimeters, 18 wells completed in bedrock, 7 wells completed in reclaimed spoil, and 2 surface- water gaging stations. The results of the study indicate that the reclaimed spoil is recharged from surface recharge and underburden aquifers. Discharge, as measured by lysimeters, was about 3 inches per year and occurred
during and after snowmelt. Hydraulic-head measurements indicated a potential for ground-water movement from deeper to shallower aquifers. Water levels rose in the reclaimed-spoil aquifer and spring discharge at the toe of the spoil slopes increased rapidly in response to snowmelt. Water chemistry, stable isotopes, geochemical models, and mass-balance calculations indicate that surface recharge and the underburden aquifers each contribute about 50 percent of the water to the reclaimed-spoil aquifers. Geochemical information indicates that pyrite oxidation and dissolution of carbonate and efflorescent sulfate minerals control the water chemistry of the reclaimed-spoil aquifer.

DESCRIPTION AND FILED ANALYSIS OF A COUPLED GROUND-WATER/ SURFACE-WATER FLOW MODEL (MODFLOW/BRANCH) WITH MODIFICATIONS FOR STRUCTURES AND WETLANDS IN SOUTHERN DADE COUNTY, FLORIDA

Swain, E.D.; Barbara Howie; Joann Fontana

USGS Water-Resources Investigations Report 96-4118, 67 pp, 1996

A coupled surface-water model (BRANCH) and ground-water model (MODFLOW) model were tested to simulate the interacting wetlands/surface-water/ ground-water system of southern Dade County. Several options created for the MODFLOW ground- ground-water model were used in representing this field situation. The primary option is the MODBRANCH interfacing software, which allows leakage to be accounted for between the MODFLOW ground-water model and the BRANCH dynamic model for simulation of flow in an interconnected network of open channels. A modification to an existing software routine, which is referred to as BCF2, allows cells in MODFLOW to rewet when dry—a requirement in representing the seasonal wetlands in Dade County. A companion to BCF2 is the modified evapotranspiration routine EVT2. The EVT2 routine changes the cells where

evapotranspiration occurs, depending on which cells are wet. The Streamlink package represents direct connections between the canals and wetlands at locations where canals open directly into overland flow. Within the BRANCH model, the capability to represent the numerous hydraulic structures, gated spillways, gated culverts, and pumps was added. The application of these modifications to model surface-water/ground-water interactions in southern Dade County demonstrated the usefulness of the coupled MODFLOW/BRANCH model. Ground-water and surface-water flows are both simulated with dynamic models. Flow exchange between models, intermittent wetting and drying, evapotranspiration, and hydraulic structure operations are all represented appropriately.

ISOTOPE INVESTIGATIONS ON THE INTERACTION BETWEEN GROUND AND SURFACE WATER IN DEVELOPING MINING LAKES
Trettin, R.; K. Freyer; G. Strauch; H.-G. Treutler; W. Glasser
UFZ-Umweltforschungszentrum Leipzig, Sektion Hydrogeologie, Halle, Germany
Grundwasser, Vol 4 No 1, p 3-10, 1999

Environmental isotopes of radon were applied to characterize relationships within and between ground and surface waters in two developing mining lakes. Using a two-component-model the portion of saline waters ascending through the lake bottom into the lakes was estimated. Similarly the contribution of pyritic sulphur participating in the lake sulfate has been assessed. Locally, the lakes are hydrochemically stratified. Mixing processes are reflected by all isotopes mentioned above. All values of the most mineralized lake water did not correspond with those of deep groundwater from Zechstein strata revailing additional effects such as CO_2 production. Radon-222 was checked for assessing groundwater fluxes through the lake bottom and was found in lake water regions with elevated salt contents but being always in an equilibrium with radium (excepting the sediment-lake water interface). Thus, radium must be taken in consideration in order to interpret radon values in saline groundwaters.

WATER QUALITY AND POLLUTION POTENTIAL OF ABANDONED GRAVEL PITS IN THE BRAZOS RIVER ALLUVIAL AQUIFER, WACO, TEXAS
Ward, Sonya Yvette, Triegel & Associates Inc., Berwyn, PA
AWRA/et al Effects of Human-Induced Changes on Hydrological Systems Symposium,26-29 June 1994, Jackson Hole, WY. p 985-994, 1994

The Brazos alluvial aquifer, located in central and southeast Texas, is used for livestock, agriculture, and domestic consumption. The alluvial deposits have been mined for many years as a source of sand and gravel, resulting in gravel-pit lakes. The possible interaction of surface water and groundwater through three of these gravel-pit lakes in the vicinity of Waco was examined. Piezometers were installed to evaluate the groundwater gradient, and water samples were collected and analyzed for common ions, pH, specific conductance, temperature, BOD, and COD. Each site is described. Overall results indicated that the lakes receive groundwater recharge from, and subsequently discharge to, the aquifer, making them flow-through in nature. Water quality of the lakes is generally within acceptable parameters. However, the sites of the lakes, which are surrounded by feed lots, offer the opportunity for nonpoint-source pollution, a situation that will become more critical as urbanization continues.

GROUND WATER AND SURFACE WATER: A SINGLE RESOURCE
Winter, T.C.; J.W. Harvey; O.L. Franke; W.A. Alley

U.S. Geological Survey Circular 1139, 79 pp, 1998

As the Nation's concerns over water resources and the environment increase, the importance of considering ground water and surface water as a single resource has become increasingly evident. Issues related to water supply, water quality, and degradation of aquatic environments are reported on frequently. The interaction of ground water and surface water has been shown to be a significant concern in many of these issues. For example, contaminated aquifers that discharge to streams can result in long-term contamination of surface water; conversely, streams can be a major source of contamination to aquifers. Surface water commonly is hydraulically connected to ground water, but the interactions are difficult to observe and measure and commonly have been ignored in water-management considerations and policies. Many natural processes and human activities affect the interactions of ground water and surface water. The purpose of this report is to present our current understanding of these processes and activities as well as limitations in our knowledge and ability to characterize them. The report is available at http://water.usgs.gov/pubs/circ/circ1139/