

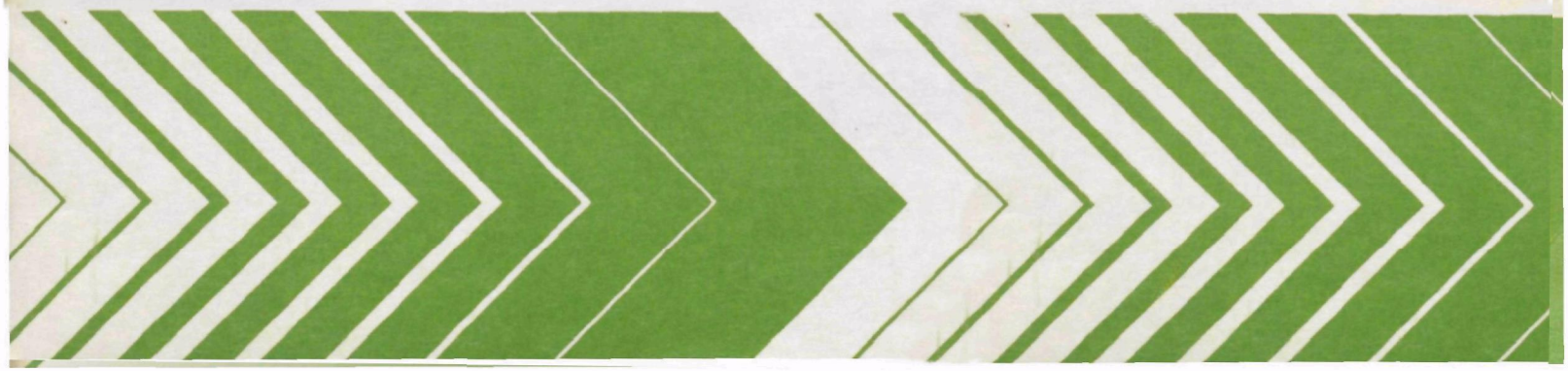
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Application of a Water Quality Assessment Modeling System at a Superfund Site



**APPLICATION OF A WATER QUALITY ASSESSMENT
MODELING SYSTEM AT A SUPERFUND SITE**

by

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FOREWORD

EPA's Center for Exposure Assessment Modeling (CEAM) was established in July 1987 to meet the scientific and technical exposure assessment needs of EPA's Program and Regional Offices and Superfund Technology Support Center for Exposure and Ecorisk Assessment. The Center is also the focal point for a variety of general Agency support activities related to the scientifically defensible application of state-of-the-art exposure assessment technology for environmental risk-based decisions. CEAM provides analysts and decision-makers operating under various legislative mandates with relevant exposure assessment technology, training and consultation, technical assistance, and demonstration of new or innovative applications. This research report describes one such demonstration project - analysis of metals contamination of the Upper Clark Fork River, Montana.

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ABSTRACT

Water quality modeling and related exposure assessments at a Superfund site, Silver Bow Creek-Clark Fork River in Montana, demonstrate the capability to predict the fate of mining waste pollutants in the environment. A linked assessment system -- consisting of hydrology and erosion, river hydraulics, surface water quality, metal speciation, non-point source and groundwater mixing and transport models--has been applied at the site to show the applicability of such modeling schemes and the complexities involved in the application. Some of the models had to be modified to match the requirements of this project. Graphs of the water quality parameters show good fit between the measured and predicted concentrations at some stations whereas substantial deviations are observed at other stations along the course of the stream.

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SECTION 1

INTRODUCTION

This project was initiated to analyze the hydrology and water quality of the Silver Bow Creek and the Upper Clark Fork River, Montana, in response to years of mining activity in the surrounding areas. Heavy metal concentrations in the surface and subsurface waters of the Clark Fork River basin have diminished aquatic life in many of the region's streams. The principal sources of these metals are the waste byproducts of copper mining in the Silver Bow Creek watershed above and around the town of Butte, Montana. One of the Superfund site, the Silver Bow Creek/Butte Area site, includes the Butte mining areas, Silver Bow Creek, the Warm Springs Ponds, and the Upper Clark Ford River down to the entrance of Milltown Dam. The other Superfund site is the Anaconda Smelter site. The Anaconda Smelter site includes the Anaconda Smelter, the surrounding waste and slag dumps, the Anaconda Ponds, and the Opportunity Ponds. A Superfund remedial investigation has been conducted for the Silver Bow Creek/Butte Area site and a set of volumes that constitute the Silver Bow Creek Remedial Investigation Final Report (RIFR) have been used as our primary references (Tuesday et al., 1987).

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The copper concentrations in discharges from the Warm Springs Ponds and the concentrations in Silver Bow Creek (WASP4 Surface Water Segments 1-7) have been simulated with accuracy, as shown in the results for Segment 1. The variance between the measured total copper concentrations in winter flood waters in the Upper Clark Fork River and the predictions in Segment 8 to 11 obtained using the methods and models described in this report, show that, for the main stem of the Clark Fork River, copper in the river may have unidentified sources currently not included within the model.

For example, the stream bed may hold a large reserve of tailings deposited during floods that bypassed the Warm Springs Ponds or deposited during floods and high flows before these ponds were constructed. Resuspension of stream-bed sediments that carry heavy metal contaminants may be the primary contaminant source if flood flows have sufficient hydraulic power to strip away the armored (cemented with lime and iron oxide flocs) cobbled (cemented over large rocks) bottom of the river and resuspend the sediments. The primary metal source during large flows and floods may be resuspended copper oxide-iron oxide precipitates, sulfide tailing particles, and copper adsorbed to iron oxide precipitates and to primary alumino-silicate sands.

It has been reported that flows in winter include ice flows and phenomena characteristic of unstable stream beds such as "head cutting" or large-scale bank erosion. The stream bed of both Silver Bow Creek and the Clark Fork River down to the town of Deer Lodge have been extensively reengineered and straightened during road construction, railroad construction, and possibly during the construction of the Warm Springs Ponds (Gary Ingman, personal communication 1989). The stream bed may be unstable during large flows and the stream bed may be widening with successive flooding events. This may cause the stream bed to widen sufficiently to reenter the older sections of the stream bed, causing further instabilities in the stream flow path and stream banks.

During winter floods, major changes occur to the transport patterns when the subsurface is frozen. Freezing of the subsurface reduces infiltration, creates ice lenses, and affects the chemical and microbiological activity in the frost zone. These phenomena are not included in the chemical transport model used (PRZM). Therefore, the runoff in winter should include a much larger portion of the snowfall, rainfall, and snowmelt than is currently predicted, and a larger runoff could result in a narrowing of the hydrograph for the winter floods.

A narrow hydrograph may lead to concentration versus time peaks that are sharper than the 1-day resolution permitted by PRZM. Concentration may vary significantly over a single day for cases when the hydrograph is narrow. An improvement in model resolution to time scales of less than a day may be necessary for such cases.

We also can conclude that there may be substantial contaminant transport events in the river that have not been looked for previously. This conclusion is suggested by the fall and late summer surface water model results. The model, therefore, could be used to plan river sampling for heavy metals, sulfates, metal-bearing colloids, sediments, and other components.

Resuspension of sediments in the Warm Springs Ponds is accounted for with constant first-order metal removal efficiencies. With current data it is difficult to determine causation in the metal removal efficiencies in the ponds, although general trends can be inferred by regression against the metal removal data. These regressions indicate that pond efficiencies increase with pH and decrease with exit flow from Pond 2, with the confidence levels for the regression coefficients being highest for the correlation of copper and zinc removal to the pH of Pond 2 effluent.

The exposure model could be extended to the other metals present in the river. Although copper is the metal most in exceedance of acute toxicity concentrations in stream surface waters below the Warm Springs Ponds at the start of the Upper Clark Fork River, zinc regularly exceeds acute toxicity standards in Pond 2 and 3. Arsenic also is present in the stream and in groundwater, so application of the exposure model to these other heavy metals would be useful. For extension to zinc, arsenic, and cadmium, data such as K_d for the groundwater in the oxidation layer would be needed. The pond removal efficiencies for zinc, arsenic, and cadmium also would be needed. Data are not available for other contaminants present in groundwater (silver, antimony, cobalt, lead).

Pond efficiencies in this model have been approximated by an average value. The seasonal determinants of pond efficiencies and the dependence of pond metal removal efficiency on flow and pH are not understood well enough to incorporate efficiency predictions into the metals loading model.

To predict the ratio of dissolved to suspended metal concentrations in the stream, pH data and information about the dependence of K_d on pH would be needed. If chemical equilibrium is assumed, these relationships could be predicted by use of an option for variable K_d within the surface water model and by use of a predictive mechanism for pH that accounts for carbonate balances and acid loadings over the stream course.

One suggestion and conclusion for improving the quality and predictive power of the modeling system is to modify the program GCTRAN, which represents large colloid transport in groundwater. If improvements are made in estimating the rate of groundwater discharge to the stream, infiltration, changes in the water table, and the effect of bank storage and evapotranspiration, then a more accurate simulation of the streamside contaminant sources may improve the predictive capability of this modeling system.

The goal of improving prediction of contaminant transport raises the need for a software linkage between surface and ground waters based on: (1) better equations of flow in groundwater and surface water for this site; (2) improved equations that define the rates of infiltration from the surface to the groundwater; (3) equations that define kinetics of particle oxidation and changes in metal form, including changes in contaminant distribution and form over different particle sizes, changes in contaminant distribution and form over different particle structures (porosity, morphology), and changes in contaminant metal distribution and form over different compositions of the particles to which the metal attaches (such as sulfides, quartz, limestone, iron oxide, mixed silicon and aluminum oxides (clays)); and (4) expanded equations that describe the effect of groundwater flow on the movement of contaminants in solution, in suspensions and within immobile solids. Having a software linkage would be a great advantage on any other project where the transport and flow in the saturated zone and in a variably porous and conductive subsurface controls the release of contaminants.

SECTION 3

BACKGROUND

DESCRIPTION OF THE STUDY AREA

Silver Bow Creek is located in southwest Montana, where it flows as a small stream from the Metro Storm Drain northwest of the city of Butte to the Warm Springs Ponds 27 miles downstream (Figure 1). Its confluence with Warm Springs Creek near Warm Springs and Anaconda just below Warm Spring Pond 2 forms the Upper Clark Fork River. Several small streams and gulches feed the creek between Butte and Warm Springs.

The drainage area of Silver Bow Creek is on the order of 425 square miles. Both acidic mine drainage and contaminated groundwater seepages enter Silver Bow Creek within the Butte town limits before reaching the Colorado Tailings. Below the town boundary, the creek continues to pass large streamside tailings deposits and flood-deposited tailings banks.

Some small tributaries, including Missoula Gulch, Brown's Gulch, and German Gulch, flow into Silver Bow Creek above the Warm Springs Ponds, a series of three settling ponds. The creek flows through Warm Springs Pond 3 (100 hectares of open water) into Pond 2 (32 hectares of open water) and into a small set of subsidiary Wildlife Ponds. The lower ponds, including Pond 1 (8 hectares of open water) are nearly filled with sediment and sediment islands break the water surface of Pond 2 and the Wildlife Ponds. Below Pond 2 the creek merges with the Mill-Willow Bypass, which drains Mill and Willow Creek and some of the waste subsites surrounding the Anaconda Smelter and the seepage from the Warm Spring Ponds and the Opportunity Ponds. Below this confluence, the creek combines with the flow from Warm Springs Creek (which drains the remaining Anaconda waste subsites) and becomes the Upper Clark Fork River. Modesty Creek, Lost Creek, Dempsey Creek and Racetrack Creek increase the river flow between the Warm Springs Creek and Deer Lodge.

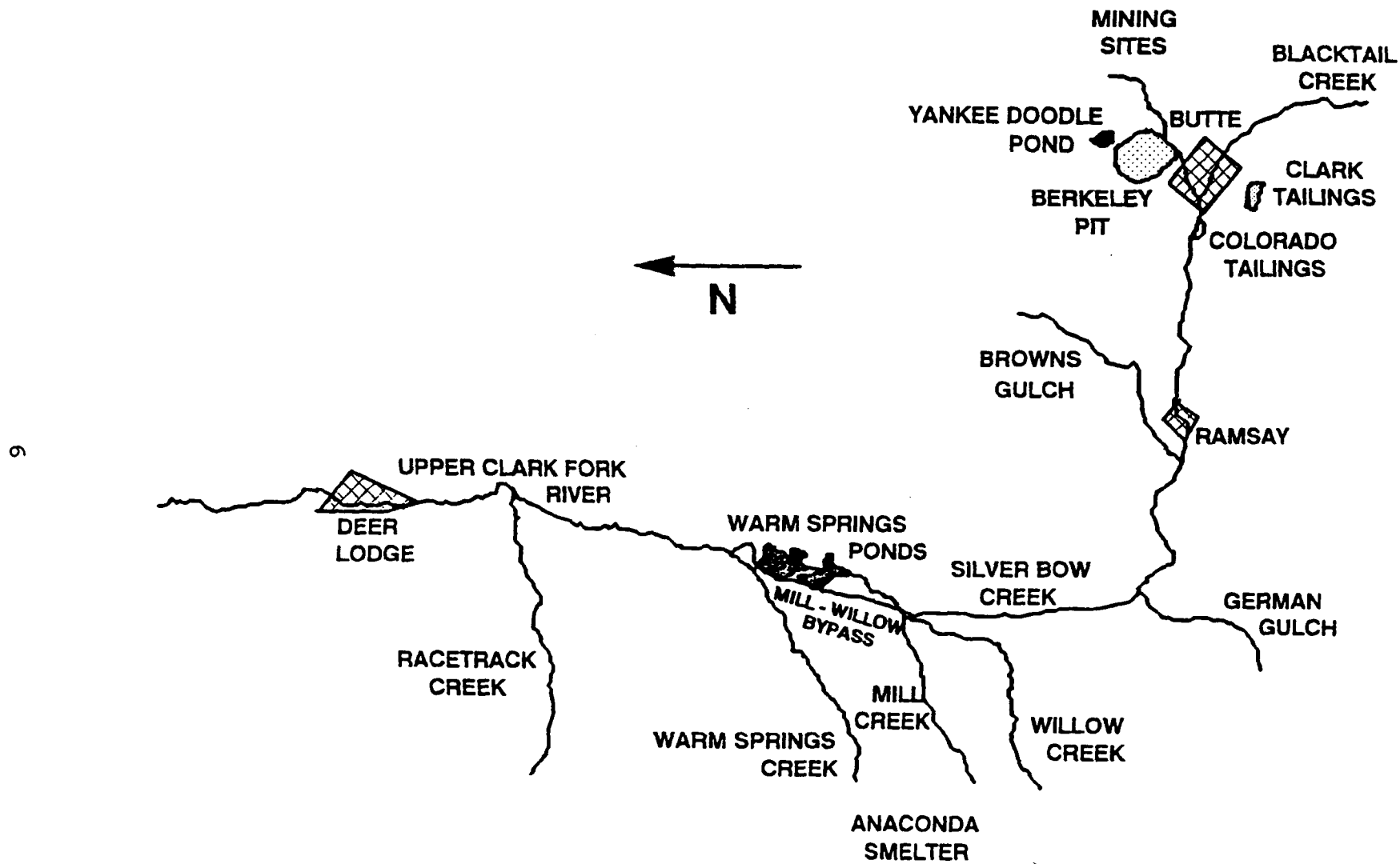


Figure 1. Upper Clark Fork basin of Silver Bow Creek, MT, a Superfund site.

More than 100 years of continuous mining operations and related activities have changed the area's natural environment greatly. Waste rocks, ore process tailings, acidic mine drainage and smelting wastes are the primary sources of heavy metal loadings to the Silver Bow Creek and Clark Fork River via surface runoff and ground water flow. The Warm Springs settling ponds have a limited volume and during high stream flows (discharges of greater than 700 ft³/sec) the Warm Springs Ponds are bypassed into the Mill-Willow Bypass without any treatment. The Ponds also may be bypassed by flows as low as 150 ft³/sec if the entry gate into Pond 3 is blocked by debris. Further, geotechnical studies have revealed that a flow of 4000 ft³/sec can result in the failure of diversion and control structures such that a large amount of contaminated sediments are released into the Clark Fork River. Hydrological investigations estimate the 100-year flood to be 3600 ft³/sec (CH2M-Hill 1988). The RIFR indicates that the seepage from under the Warm Springs Ponds can act as a major source of ground water pollution. Toxic elements within tailing deposits include arsenic, cadmium, copper, lead, iron, and zinc. The severity of the contamination problem was such that, in 1983, EPA declared the area along the course of the Silver Bow Creek and Clark Fork River from Butte to the Milltown Dam to be a high priority Superfund site. The site hydrology, hydrogeology and geochemistry are very complex due to the variety and magnitude of contaminant sources and the multitude of pathways to the surface water and ground water resources. Therefore, a detailed modeling scheme was employed to delineate the pathways and the fate of pollutants.

HISTORY OF METALS IN THE RIVER

Since 1880, when large scale mining and smelting of copper began, the valley and the stream have been used as dumping areas for wastes. Wastes in Butte include tailings from the flotation process that separates copper from the ore and waste rock that was removed as backfill and overburden, or, was discarded as being too low-grade to be put through a separator.

Pollution problems began early along the Silver Bow Creek. The first industrial operations sluiced the wastes directly into the stream. Later, the mine operators constructed settling ponds and streamside tailings piles as part of an attempt to preserve water quality. The wastes in the stream moved down the river, especially during floods which caused erosion and transport of sediment, and were widely distributed over the flood plain and the river bed, at least as far as Milltown Reservoir (below Deer Lodge).

In 1911 and 1916, Warm Springs Ponds 1 and 2 were constructed on Silver Bow Creek above the confluence of Silver Bow Creek with its two principal tributaries, Warm Springs Creek and Mill-Willow

Creek. The height of Warm Springs Pond 2 was raised during 1967-1969. These ponds originally were designed to settle the metals carried by Silver Bow Creek and prevent contamination further downstream.

As the two ponds lost capacity due to sediment accumulation, sedimentation efficiency declined and more particles remained suspended in the effluent and were carried into the river. To remedy the problem, Warm Springs Pond 3 was constructed above the first two ponds between 1954 and 1959. Pond 3 was improved between 1959 and 1969 to increase the capacity for metal removal.

Beginning in 1967, lime has been added to the ponds to precipitate and flocculate the heavy metal contaminants that enter with the stream flow. This method of settling the metal colloids and particles from Silver Bow Creek has been successful in reducing the metal content of the Clark Fork River during periods of normal flow. During high flows, however, the ponds are bypassed and Silver Bow Creek enters the upper Clark Fork River without treatment.

Between 1933 and 1937 the stream itself was channelized to prevent further erosion of the tailings from the banks. The first alteration to the stream course of the Silver Bow Creek was a channelization of the flow between smelter slag blocks placed along the stream channel. This was done to prevent the downstream transport of newly deposited mine and slag tailings on the old banks during periods of bank overflow due to flooding.

BIOLOGICAL IMPAIRMENT

Adjacent to Silver Bow Creek and the Clark Fork River are flood plains and low banks that have been covered with waste sediments. Silver Bow Creek in its natural state was a meandering brook through lush marshes and wetlands. The original environment included wetland bogs, moss banks, and a rich floral habitat that may have supported a wide variety of higher invertebrates (for example, crayfish), fragile aquatic and wetland plants, salamanders, turtles, and wetland-nesting birds. In many places in the Upper Clark Fork River Basin, below the flood-deposited gravel and mine waste is a thick layer of organic material, bearing evidence to the original biological diversity and richness of the basin.

In some areas, heavy metals from the sediments have either limited plant growth to metal-tolerant species or killed entire plant communities. These areas are called slickens, a term that applies to all of the areas that are either dead or have visible biological impairment. The past use of water from the Clark Fork River for irrigation has led to the contamination of grazing lands.

The biological habitat within the river and creek has been damaged as well. Silver Bow Creek does not support trout, whereas

the Upper Clark Fork River supports a brown trout population that suffers from both chronic and acute toxicity. The river always contains significant metal toxicants, such as zinc, copper, arsenic, lead, cadmium, and aluminum.

Mass fish kills occur during floods, and the acute toxicity of the stream due to elevated metals concentrations is thought to be the cause. During flood flows (which can occur during late winter snow melts and during early and late summer heavy rain storms), flow in Silver Bow Creek can bypass the Warm Springs Ponds and enter the Upper Clark Fork River. Such events are known to have caused mass fish kills in the Clark Fork River.

HAZARDOUS WASTE INVENTORIES IN THE UPPER CLARK FORK BASIN

The following waste inventory includes, from the top of the basin to the town of Deer Lodge, the major waste subsites, the area of coverage, the volume and mass of waste, the type of waste, and the history of each subsite.

The conversions used were as follows. One hectare is 2.47 acres. The approximate density of the mill tailings(wet) used in the RIFR is 2.6 g/cm^3 , or 2700 pounds/yd³. This density is equivalent to 1.35 tons per yd³. One pound is 0.454 kg, and one ton is 0.908 metric tonnes.

Although the effects of the seepage from the Berkeley Pit (in the Butte Operations Active Mine Area) and the 500 mines and shafts (with 3000 miles of underground workings) in Butte and the vicinity are severe and contribute greatly to contamination, we have no way currently of predicting the time dependence of those effects. Consequently, we have focused on estimating the mass of the known waste subsites above ground.

As a rough estimate, the overall average mass fraction of remaining copper in the tailings and waste materials is assumed to be 2080 mg/kg of bulk waste material, or 0.208% by weight.

Estimates for copper content in uncovered streamside mill tailings impoundments can be made based on the Colorado Tailings total mass fraction of copper(1829 mg/kg). The mass fraction of copper in fluvially mixed streamside tailings deposits is approximately 2350 mg/kg (RIFR Summary). The estimate of average measured solid phase tailings concentrations of copper in tailings in the Opportunity Ponds is 2030 mg/kg of bulk waste material, or 0.203% by weight (Tetra Tech, 1985).

The largest waste holding in the Upper Clark Fork River Basin is the collection of waste dumps and leach pads in and around the Butte Operations Active Mine Area in Butte. The area of coverage is 1400 acres or 567 hectares. The waste mass is approximately

9.08×10^{11} kg, and is composed of mine waste rock, mill tailings, and heap leach tailings.

The second largest dump site in the Upper Clark Fork Basin is the Yankee Doodle Tailings and its tailings dam, in the Butte Operations Active Mine Area, which has 2.27×10^{11} kg of waste material and impounded tailings. This subsite covers 750 acres (304 ha).

In Butte and the vicinity, there are 150 major unreclaimed and reclaimed waste rock dumps, totaling 350 acres (141 ha) in area. The volume is estimated to be 9.85×10^6 yd³, equivalent to a mass of 1.21×10^{10} kg, which represents the fifth largest repository for waste in the Upper Clark Fork River basin (Camp, Dresser, and McKee, 1987).

Butte and vicinity also include small side-stream tailings deposits that include the Colorado Tailings (30 acres, 2.5×10^5 yd³) and the Clark Tailings (62 acres, 1.0×10^6 yd³).

Along Silver Bow Creek from Warm Springs to Deer Lodge, it has been estimated that there are 4.25×10^6 yd³ of waste material (equivalent to a mass of 5.21×10^9 kg. This material includes mixed tailings, mine waste rock, natural sediments, and precipitates. This waste has been mapped based upon the visible portions, and the visible area is 1100 acres (445 ha).

The RIFR describes the Warm Springs Ponds as being estimated to contain "approximately 19 million cubic yards of mixed tailings, mine waste rock, natural sediments, and precipitates" (based on study by Hydrometrics, 1983). This volume is equivalent to a mass of 2.33×10^{10} kg of waste. This mass estimate ranks the wastes in the Warm Springs Ponds as the fourth largest waste repository in the Upper Clark Fork River basin. The surface area that these wastes cover is the total area of the Warm Springs Ponds plus the dried pond beds (Pond 1 and 2) and is a minimum of 346 acres (140 ha).

The third largest mass of waste at a subsite is at the Anaconda Smelter site. Initial estimates of the waste mass at the Anaconda Smelter (smelter wastes) and the Opportunity Ponds place the figure for contaminants at 1.85×10^8 yd³ (equivalent to a mass of 2.27×10^{11} kg) and the Opportunity Ponds surface area coverage at 6000 acres (2428 ha) (Tetra Tech, 1985). Additional Anaconda site wastes are at the Old Works near Warm Springs Creek and at the Anaconda Ponds.

The above listing of known subsites may be incomplete, but will be amended if more subsites become known, such as other subsites in and around Anaconda. The approximate total mass of copper mining, beneficiation, and smelter waste materials is 1.41×10^{12} kg.

SECTION 4

OBJECTIVES

The modeling effort at the Center for Exposure Assessment Modeling (CEAM) focused on the prediction of the frequencies of exposure of fish to toxic metals at different concentration levels in the stream by using metal speciation and water quality models combined with historical data on the site. Investigations to date have focused on the typical flood events. The main objective is to complete a description of metals exposures and anticipated effects on the entire river during historical periods of flooding. The mechanisms affecting the native fish, including the exposure time(s) and concentrations that produce mortality, will be modeled by EPA's Environmental Research Laboratory, Duluth, Minn. (ERL-Duluth).

SECTION 5

MODELS AND METHODS

The general conceptual model describes sources of various metals (species) in waste dumps and on the river banks.

Chemical partitioning between water and soil during transport and transformation of heavy metals into the stream were analyzed in the following manner as indicated in Figure 2. The chemistry of the tailings deposits was used to determine the form of the metals; the flow behavior of rain on the banks as well as overland flow determined the principal transport mechanisms. The rates of metal transport depend on the rate of advection predicted by PRZM (Carsel et al., 1984), GCTRAN, and NPSOUT (Brown, 1989) and the solubility of the oxidized metal at sulfide particle surfaces indicated by MINTEQA2 (Brown and Allison, 1987). Surface water transport is simulated by WASP4. The hydraulic parameters for WASP4 (Ambrose et al. 1987) are provided by a river hydrodynamic and sediment transport model RIVERMOD (Hosseini pour, 1988b). The toxicity evaluations will be performed by a Fish Acute Toxicity model developed at the ERL-Duluth.

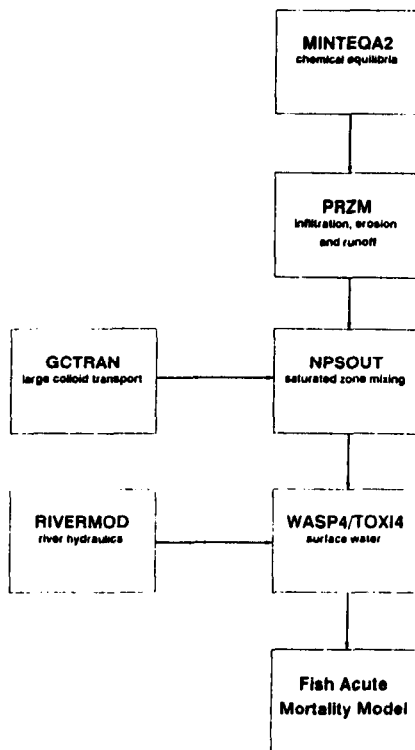


Figure 2. Diagram of modeling system used in Clark Fork River exposure assessment.

SITE GEOLOGY AND GEOCHEMISTRY

The Superfund site has been divided into geographic subsites for the purpose of exposure assessment modeling, with each subsite having its own geology, hydrology, and geochemistry. The processes that create acidic effluent from mine solid wastes are summarized below.

The ores are blasted from the rock face, mined, and crushed. The crushed ore is then processed by beneficiation, which is a floatation separation that removes copper minerals from the remainder of the ore. The tailings are wastes from beneficiation that are predominantly wet finely crushed rock with floatation chemicals (predominantly sulfonated pine oils) adhering to the rock surfaces. Mechanical reduction in size of the ore particles that is intended to aid flotation-separation (beneficiation) of concentrate from tailings results in an increase in surface area available for oxidation of the remaining metal sulfide minerals in the tailings. Waste waters from the beneficiation process include sulfate, metals, and beneficiation chemicals in solution or emulsion. The copper minerals are smelted in an oxidative roasting process that produces copper metal; slag is left as process waste.

The streamside tailings deposits are sand-like fine particles of metal sulfides embedded in feldspar and quartz. The primary metal sulfide minerals in the waste rock, overburden, and processed ore include iron pyrite (FeS_2 , iron sulfide), chalcopyrite (FeCuS_2 , iron-copper sulfide), realgar (AsS , arsenic sulfide), chalcocite (Cu_2S , copper sulfide), and galena (PbS , lead sulfide). These minerals originally were geologically embedded in monzonite porphyry formations. The metal sulfide deposits were formed by sequential hydrothermal precipitations; sulfides were deposited from hot geothermal solutions. As the geothermal solutions flow from hot rock into rock fractures at lower temperatures, the solutions drop in temperature and become supersaturated. The deposition of sulfide occurred on the surrounding parent rock surfaces and in rock fissures.

The sources of the copper to the creek and river are waste copper sulfide-bearing particles that are corroded by exposure to water and oxygen. The limits on metal transport and solubility will determine the magnitude of sources of contaminants to the river. Under certain circumstances the partitioning of metal between waste materials and water can be simulated with MINTEQA2. MINTEQA2 is applied with the assumption that oxidized heavy metal is always present (metal availability is not rate-limited). Eh is set by the balance between oxygen diffusion and consumption, and decreases with soil and waste material depth. pH is set by advection and diffusion of H^+ away from the particle. pH is decreased by limitations on diffusive and advective transport of hydrogen ions and

this increases the diffusive driving forces for oxidized metals. pH increases with depth: with less oxygen, less H^+ is created because of the lower oxidation rate.

Oxygen Transport

Eh is controlled by the availability of oxygen. The metal sulfides in tailings react with oxygen and water to form metal ions (Fe^{3+} , Cu^{2+}), and sulfuric acid (H_2SO_4). The process of oxidation depends on a supply of reactants (water, sulfides, oxygen) and on water as a transport medium for reactants and products. The process of oxidation in nature or in deposits of waste materials is limited by transport of product or reactants; otherwise metal sulfides would not be frequently observed in a natural or disturbed setting.

Oxygen is transported from the ground surface of the tailings where oxygen in the water phase is in equilibrium with the atmosphere. Oxygen diffuses into the tailing deposit on the stream bank and is transported by diffusion and advection into each unsaturated soil stratum where sulfides are present. Transport of oxygen to the metal sulfide particle core depends on the rate of diffusion through metal oxide and metal sulfate layers on a particle surface. The rate of metal oxidation and sulfate formation is assumed to be equivalent to the oxygen transport rate through the soil pores (that is, the oxygen transport rate is assumed to be the rate-limiting step).

The rate of oxygen transport into the oxidized layer and through the sulfide particle fissures to unreacted metal sulfides is greater than or equal to the transport away of some oxidation products (FeO or CuO). This was concluded from the observed buildup of metal oxides on particles in the oxidized soil stratum of the saturated zone.

Oxidation Product Transport

As the sulfides are oxidized and byproducts (such as the sulfates, the oxides, sulfuric acid (H_2SO_4), and H^+) build up, they must be carried away in order to prevent a halt to oxidation. As corrosion of the sulfide proceeds, the pH of the particle surface drops and the copper at the particle surface and within particle fractures and crevices becomes more soluble. Oxidation products are transported away by diffusion out of the particle fissures into the soil pore water and subsequent advection. If this did not occur, oxidation products (H^+ , SO_4^{2-}) would build up and hinder oxidation kinetics and thermodynamics. Some oxidation products (H^+ , SO_4^{2-}) will be removed faster than others (solid CuO , FeO), and so a buildup of some products (metal oxides, carbonates, and sulfates) occurs at the oxidation front between solid oxidized metal and metal sulfides. The rate of accumulation of waste products at the oxidation front is determined by the kinetics of oxidation and by

the reaction-limiting mechanisms for transport of products and reactants (Figure 3).

Copper diffuses into the groundwater and enters other transport pathways. The oxidizing particles are the major source for copper entering subsequent transport pathways such as runoff, erosion, and leaching. Less dilution of acid occurs during dry periods, so that the H^+ ion is trapped and increases the solubility of oxidized metal. Consequently, during dry periods, there is an increase in the mobility of particulate and soluble metal outside the tailings particles. During wet periods, pH at the particle surface is raised sufficiently to reduce transport outside the particle and reduce the source term. This can serve as an explanation why the magnitude of the source term varies seasonally and why the calibrated K_d may have a lower value during seasons that are concurrent with accumulation of oxidized metal in the pore water and on the tailings surfaces. Capillary transport of oxidized metal and acids to the tailings surface may also result in seasonally variable calibrated K_d and seasonally variable transport of metals and acids. Recent surface water analytic data that encompasses a wider range of flow and seasonal conditions should make possible the modeling of seasonally variable heavy metal transport.

The ground pore water around the sulfide particles has a lower hydrogen ion concentration than the water film around the sulfide particles, and the higher pH reduces copper solubility relative to the water film. As the copper diffuses from the sulfide particle surface to the bulk solution, pH increases and the copper can form a metal oxide or carbonate precipitate in suspension in the unsaturated zone. The pH is between 3.0 and 5.0 in the unsaturated zone of the oxidized soil layer and a pH as low as 2.5 in the water film on the surface of the oxidizing sulfide particle. The higher pH and lower Eh can cause precipitates to form in the groundwater. These precipitates may also constitute a major portion of the copper transported by leaching and underflow, and copper may be carried in colloidal form (as precipitates in suspension) in the groundwater of the saturated zone.

Dependence of Geochemistry on Soil Depth

In the absence of a one-dimensional model that will define the geochemical conditions for a vertical soil core, the first step in the analysis of the waste site is to develop a general modeling framework. The soils of the Upper Clark Fork Basin are a poorly sorted alluvium that comprises sand, silt, and gravel. The soil core can be simulated with a mixture of tailings and alluvium measuring 250 cm deep and with a water table that can vary from a depth of 0 cm adjacent to the stream bank to a depth of 250 cm at the edge of the tailings furthest away from the surface water (Figure 4).

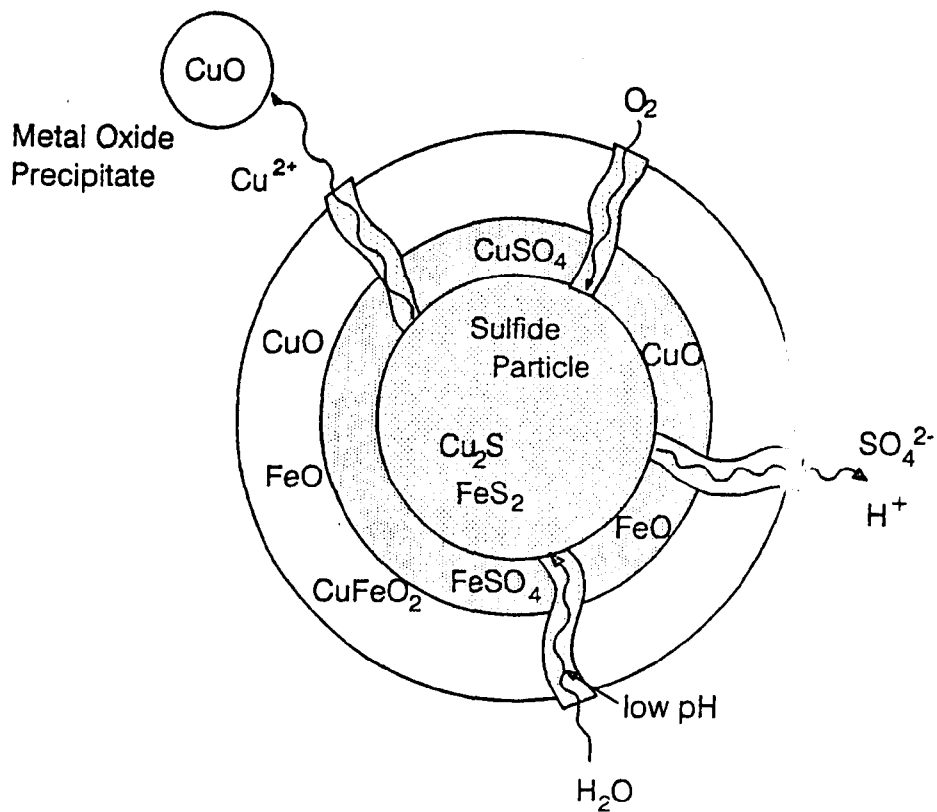


Figure 3. Oxidation of a sulfide particle.

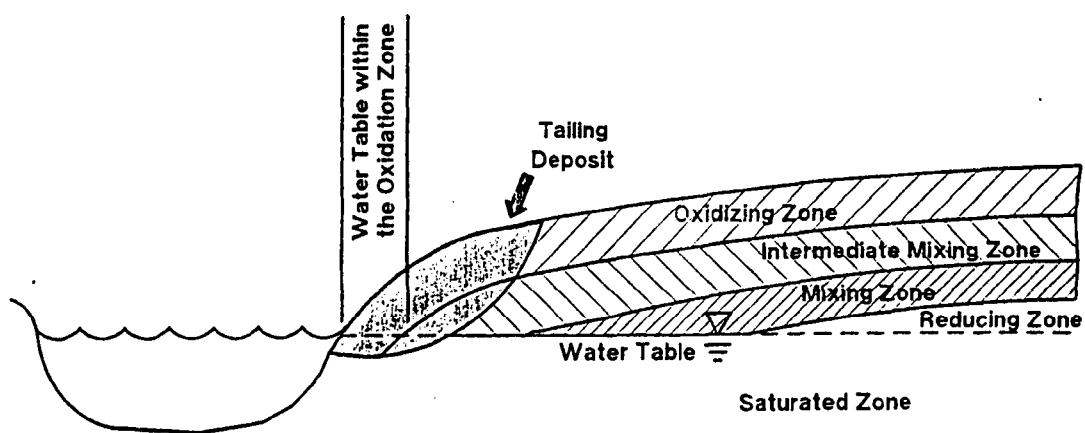


Figure 4. Profile of the river, water table and tailing deposit.

Each soil stratum below the surface of the stream-side tailings deposit is geochemically defined by the oxygen consumption and oxygen concentration in that stratum. The model for the tailings pile geochemistry that is illustrated here corresponds to both measurements of depth versus geochemistry in the Remedial Investigation Final Report (RIFR) (Tuesday et al., 1987) and other literature on mine tailings geochemistry (Tetra Tech, 1985). Oxygen diffusion to lower strata is limited by consumption in upper soil strata. Diffusion is especially limited for tailings that are compacted, fine-grained, flocculated, or that have a small void fraction. In such situations, the limited amount of diffusing oxygen can be totally consumed in the upper soil strata. (Figure 5)

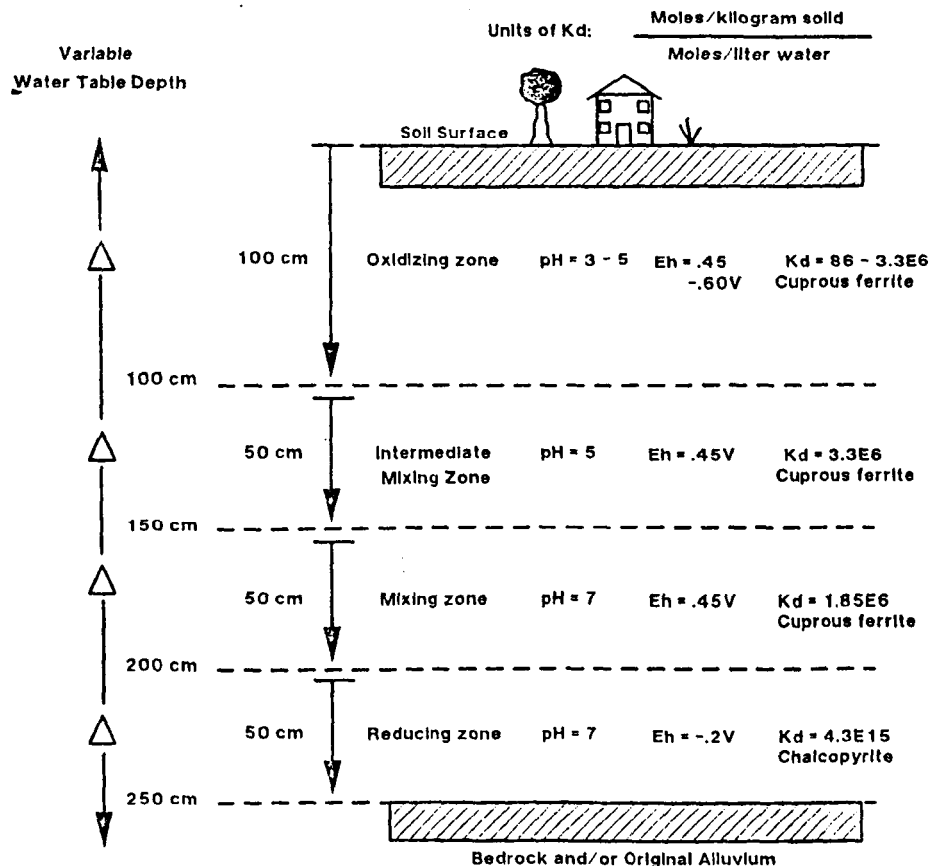


Figure 5. Geochemical profile of the unsaturated tailings and alluvium. Diagram shows the geochemical properties of the mixed tailings and alluvium when they are above the saturated water level.

In some cases the tailings have been mixed by alluvial or mechanical processes with the common bedrock of the Upper Clark Fork River basin. This native bedrock has large portions of calcium carbonate that can neutralize acid produced by oxidation and corrosion of the sulfide particles.

The conditions in the soil and tailings mixture are represented by two geochemical parameters: Eh (electrochemical potential) and pH (hydrogen ion abundance). The hypothesized vertical sequence of unsaturated tailings geochemistry is described as follows; the oxidized stratum is the top tailings layer, below which are, in sequence, the intermediate mixing layer, the mixing layer, and the reduced tailings layer (Figure 4).

The top 100 cm of the soil-tailings layer has excess oxygen available, and the Eh consequently is at an oxidizing potential of between 0.45 and 0.80 mV. Because of the rapid rate of hydrogen ion production, the pH in this layer is represented as 3.0-5.0.

The very top of the soil is subject to the most regular erosion and oxidation. It may be that the top 1 to 10 cm of tailings are completely oxidized and are not acidic. However, this has not been the assumption of the descriptions provided here. If pH was high (>5.0) at the surface, then a separate soil layer could be included in PRZM with a higher value for copper K_d . A high pH would reduce copper solubility and copper transport due to runoff. A leached surface would also have a lower mass fraction of copper and less copper available for transport by erosion. Changes in the model to represent a top tailings layer that has a high pH and a low copper content would reduce the flood-mediated transport of copper.

If capillary-driven upward movement of copper and acid results in the surface deposition of acid, copper, and other metals on the tailings surfaces then the opposite of surface leaching will occur. Evidence that this is occurring comes from the dramatic and rapid rise in the metal content and the acidity of the river during rain storms, floods, and rapid snowmelts. An input file for PRZM would represent the copper-enriched top layer as having a higher copper content and a lower K_d . In the absence of site-specific evidence neither the enriched surface or the leached surface have been represented in the PRZM input files.

The mixing layers are depicted with an electrochemical oxidation potential of approximately 0.45V. The intermediate mixing layer is between 100 and 150 cm deep and with pH=5. The mixing layer is between 150 and 200 cm and with pH=7. In these layers, the hydrogen ions mix with the reducing compounds in the soil core, but because some oxidation is still occurring, Eh remains at 0.45V. Oxidation also can occur as a result of copper sulfate oxidizing

iron sulfide to form copper sulfide and iron sulfate. Even in the presence of hydrogen ions from the oxidation layer above, the pH is higher in the mixing layer because of lower reaction rates and the neutralizing effect of the carbonates and the unoxidized sulfides.

In this simulation of native soil and tailings, the bottom layer is assumed to be a reduced stratum, where there is a negligible concentration of oxygen. The bottom soil layer has the least oxygen available and considerable reserves of reducing sulfide, so that Eh is in a reducing range ($Eh = -0.2V$, $pH = 7$).

The saturated zone has little oxygen because of oxygen consumption by reaction in the upper layers and because diffusive transport through water is slow. Oxidative conversion of sulfides in the saturation zone, therefore, is assumed to be small relative to the oxidation rate in the unsaturated zone. The saturated zone is better mixed than the unsaturated zone because of the continuous water phase. The Eh value is between -0.2 and 0.2 V, and pH is between 6.5 and 7.5.

Geochemistry Controls Leachate

Depending on the depth of the water table and the width of the tailings deposits, leachate will either pass only through the shallow oxidized layer or will penetrate more deeply into the mixing and reducing layers. The water table level affects the quality of the leachate entering the water table and helps determine the form and the concentrations of metals that pass into the stream.

To characterize the leachate that enters the water table, it is necessary to determine solubilities in the last unsaturated zone soil and tailings layer and the metal concentrations in the leachate in this layer. The geochemical conditions in the last unsaturated zone layer will determine solubility, and the depth of the soil and tailings layer will dictate the approximate values of the principal parameters (Eh, pH).

If the water table is adjacent to the reduced layer of soil and tailings, the model we have proposed will predict less soluble copper in the leachate than if the saturated layer was adjacent to the oxidation layer (the top 100 cm of the soil core) or the mixing layer (the middle 100-200 cm of the soil core). We do not have data that quantifies the amount of colloidal copper transported in the unsaturated zone or in the saturated zone.

Hydrogen ions are assumed to be neutralized in the reduced layer by the metal sulfides and calcium carbonate present in the alluvium, and the pH is assumed to remain at about 7. The sulfuric acid may either be neutralized by calcium carbonate (calcareous bedrock and alluvium) or reduced by iron pyrite and other unoxidized sulfides. Metal sulfates and sulfuric acid are

precipitated and neutralized.

The water table can intercept any of the strata of the unsaturated zone, depending on the distance from the stream, the water table gradient, and the slope of the stream bank. At the edge of the stream, the water table and the soil/tailing deposit surface are the same. Away from the stream edge, the water table has a more shallow gradient than the deposit surface slope. The water table gets deeper and the water table intercepts lower geochemical strata as the distance from the stream increases. A lower slope for a stream bank has a more shallow water table (Figure 5).

The framework of a water table that intercepts the leachate from deeper unsaturated zone layers as the distance from the stream increases provides a means of evaluating the leachate loading from each of the layers. To do this, the intersecting area of each layer that is bounded by the water table needs to be evaluated. Each intersecting area represents an interface between the saturated and unsaturated zone that carries a leachate across the boundary. In order to characterize the leachate at this boundary, it is necessary to determine solubilities in the unsaturated layer and the metal concentrations in the leachate (Figure 5).

MODELING METAL SPECIATION/TRANSPORT

The needs of this project dictate that a metal speciation model be employed to predict metal solubility and that surface and subsurface flow and transport models be used to predict the rate of contaminant transport from the tailings deposit. The metal speciation model used is MINTEQA2 (Brown and Allison, 1987).

Metal Speciation Model--MINTEQA2

MINTEQA2 solves for the thermodynamic activities of all possible compounds in aqueous solution by solving iteratively the combined mass balance and mass action equations. The model uses a thermodynamic database of formation constants and reaction stoichiometries. The mass balance equations are established by the initial amount of each component in the initial mixture. Mass action equations are established by the formation constants for each metal-ligand complex. The simultaneous equations are determined by the complexes for which data exist in the thermodynamic database for a set of specified chemical components. The combined set of equations is solved using the Newton-Raphson iteration method.

In addition to solution chemistry, MINTEQA2 predicts the formation of precipitates; it also predicts adsorption of metals and the formation of metal-organic complexes when the sorption and formation constants are included in the database.

The Pesticide Root Zone Model--PRZM

The water balance on the surface and through the unsaturated zone includes precipitation, infiltration, runoff, and evapotranspiration. The flow in the unsaturated zone and on the tailing deposit surfaces may be one or more of the following: overland flooding, infiltration, underflow, and runoff from the slopes above the stream bank. Rainfall is the source of all four flows. Rainfall can either flow over the surface as runoff and cause erosion, or infiltrate and flow in the subsurface through the open pores and reach surface water flows as interflow before reaching groundwater table. It can cause overbank flooding during a flash flood or sudden snow melt, and ultimately it may percolate through the entire unsaturated zone and reach the aquifer to become deep groundwater storage and/or the underflow (baseflow) component of streams.

PRZM was developed to model the transport of pesticides in and below the root zone in agricultural fields. Flow of water across the tailings deposit surface, and through the deposit is predicted by PRZM. The PRZM model uses the Soil Conservation Service (SCS) Curve Number method to partition the precipitation between runoff, infiltration, and evaporation (Carsel et al. 1984).

The predicted contaminant transport modes in PRZM include runoff (dissolved metal carried in overland flow), erosion (metal in solid phase carried by suspension in overland flow), and leaching (gravity-driven unsaturated zone transport of soluble metal). Two modes of transport not presently modeled in PRZM are overland flood transport of metals and capillary transport of contaminants to the surface from the subsurface. Overland flood transport of metals is distinct from transport by overland flow erosion, and is similar to sediment transport in streams and rivers (see Figure 6). Capillary transport occurs when the soluble metal is carried to the surface of the soil by upward flow when evapotranspiration is occurring rapidly. The soluble metal collects at the soil crust and appears as a salt with white or green crystals of zinc and copper sulfates and carbonates.

PRZM includes the parameter, K_d , that describes the relative amount of contaminant in solid phase versus aqueous phase. This parameter is called the partition coefficient and is calibrated using stream quality data.

THE INTERFACE PROGRAMS BETWEEN PRZM AND WASP4

Calibration of PRZM was performed using data on surface water runoff from tailings sites along Silver Bow Creek and data on sediment erosion in Butte at the headwaters of Silver Bow Creek

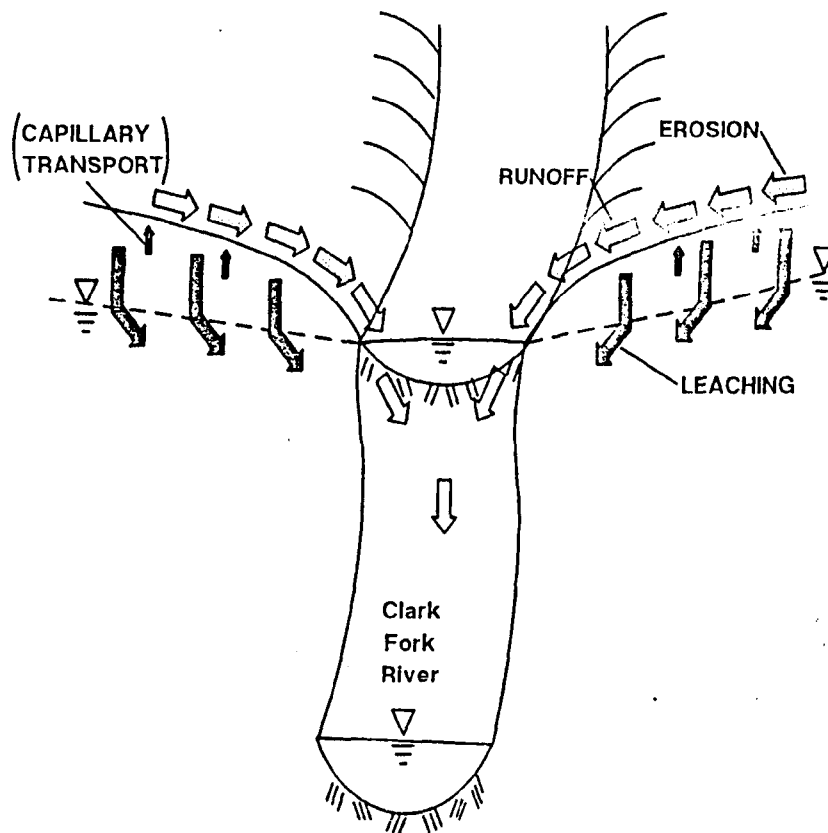


Figure 6. PRZM evaluates the magnitude of metals loading to the river for each of the three pathways.

(Brown, 1989). Using the contaminant release time series from PRZM program runs, daily releases of metals and eroded sediments can be determined for each site using NPSOUT and GCTRAN. The daily loading of copper into a surface-water transport model (WASP4) is predicted using the geography of the subsites. Output from the NPSOUT program is transferred to WASP4 as a non-point source loadings file.

These daily loadings into each portion of the river take into account measured slopes, areas, and aquifer types. For each contaminated subsite, the surface area in hectares is needed. Geographical data are sparse for the off-stream sites. The width of stream-side tailings were measured for the entire river course, and the average width of the stream-side tailings was used to calculate the area of the streamside tailings subsites. The areas of these subsites are shown in Table 1.

The NPSOUT Program

NPSOUT is a program written for this project to predict the transport of contaminant between the plant root zone and the

surface water by simulating mechanisms for contaminant transport through the near-stream saturated zone (Brown and Hosseinipour, 1989). The NPSOUT program obtains and uses output data from both PRZM and GCTRAN. PRZM output data are used to predict the movement of small particles (less than 100 nm diameter). The GCTRAN program simulates large particle generation and transport in the unsaturated and saturated zone.

Predictions of metals transport in groundwater will depend on whether the metals are in particulate or soluble form. If the metals are in particulate form, then the phenomena that affect particle mobility will become important for predicting contaminant transport. Typical pH and Eh of the saturated zone (pH about 6.5, Eh about 0.2V) indicate that the metal will be in a colloidal precipitate form. The transport of this precipitate should not be retarded by the adsorption of colloid onto the soil; the precipitates should have a very low adsorption rate, because of electrostatic stabilization.

The program NPSOUT provides metals loadings from both the streamside deposits and other sources; it adjusts the metals source magnitudes using various parameters. The principal parameters that can be modified in NPSOUT and PRZM input files to calibrate the predicted surface water concentrations to known data are the metals concentrations at the surface of the soil and tailings mixture, K_d , and the recharge flow to streamside aquifer volume ratio Q/V . Rates of transport of metal through groundwater also will depend upon the hydraulic gradients and the hydraulic conductivity of the soil through which the metals pass on the way to the river.

TABLE 1. Waste Site Areas

Location	Area (hectares)	Type of wastes
Butte surface	1049	waste rock
Butte subsurface drainage	not applicable	acid mine
Anaconda Smelter/ Opportunity Ponds	2429	smelter waste
streamside and alluvium	648	mixed tailings

The principal modes of metals transport in the saturated and unsaturated zone are transport as colloidal particles and as solutes. Colloids are a product of precipitation from oversaturated solutions. It is assumed that the smaller colloidal particles are transported by advection. One simplifying assumption is that larger

precipitates formed in the unsaturated zone are immobilized and only soluble compounds and small colloids are carried from the unsaturated zone to the saturated zone; this assumption leads to one transport model for the larger colloidal particles and another for the smaller colloidal particles.

GCTRAN output data are used to model the transport of larger particles (between 100 and 10,000 nm in diameter). The particle size division is arbitrary as there is no general theory for predicting particle size and mobility in unsaturated media during oxidation processes at this time.

One purpose of the NPSOUT program is to provide a mixing model for the transport of solutes and the smaller classes of colloids (100 nm to 1 nm) assuming a particle velocity identical to the water flow velocity in both the saturated and unsaturated zones. The rate of movement of water and contaminants in the solute and small colloid forms through the porous media (saturated and unsaturated) is assumed to be the same. The overall velocity for contaminants in the unsaturated zone may be much lower than in water because of the confined movement of large particles.

Small particle and solute transport in the groundwater is described with a Continuous Stirred Tank Reactor mixing model. Smaller particles and solutes are treated as first entering a well-mixed partial volume, V , of the aquifer and then entering the stream with a fixed flow rate, Q . The smaller particles have an average residence time in the aquifer that depends on the ratio Q/V . Calculation of Q is based on the hydraulic gradient, the hydraulic conductivity, and the stream depth. Calculation of V is based on the width of the tailings and the depth of the aquifer. Porous media flow is governed by Darcy's Law.

Q/V is the parameter that represents the ratio of the horizontal flow rate in the aquifer to the effective tailings deposit width on one side of a perennial stream (for the case of a streamside deposit) or an intermittent stream (for the case of off-stream waste subsites).

Flow gradient and aquifer permeability are measured or estimated. Average groundwater velocity can be calculated using the above parameters. Local velocities can be obtained by the solution of groundwater flow equations subject to the prevailing boundary conditions. The velocity and stream depth are used to estimate the total flow Q through the aquifer.

The approximate pulse lifetime is then chosen for the subsite. Final values are shown in Table 23.

For contaminated aquifers that are at a distance from the stream, a time of travel parameter for travel from the mixing volume in the aquifer to the streambank where recharge is released by the aquifer also can be included in NPSOUT. For all following

trials, travel time from the pulse front to the surface water has been set to 0 days, as the tailings in all cases are immediately adjacent to the surface water.

The contaminant flux into the saturated zone was determined using the leachate fluxes predicted by PRZM. The fluxes entering the groundwater are treated as entering a partial aquifer of fixed depth and a width equal to the average stream-side tailings deposit width (i.e. 38m). The parameter used within the program NPSOUT to represent the rate of decline in the contaminant concentration in the aquifer is the ratio Q/V , where Q is recharge flow per day from a partial aquifer volume and V is the maximum partial volume of the aquifer that is well-mixed.

Two trial values of Q/V are 0.4 for the streamside tailings and 0.04 for the main tailings deposits in Anaconda and Butte (based on a lower hydraulic conductivity for the off-stream sites). The difference in the parameters also could be attributed to the larger waste deposit widths, which could be much larger for the off-stream sites in Anaconda and Butte, or to greater stream depths for on-stream tailings. A value of 0.04 leads to a time scale of 120 days for complete emptying of the aquifer of a single 1-day contaminant pulse, and 0.4 to a time scale of 10 days for the same scenario. Thus the contaminant pulse lifetime does not need to exceed 120 days. Final calibrated values for Q/V are shown in Table 23.

Values for horizontal velocity of 900 to 3650 ft/year (0.75 to 3.0m/day) have been reported (Tetra Tech, 1985) in the Opportunity Ponds alluvial aquifer (with a hydraulic gradient of 1%). These flows are in a northeast direction, towards the Mill-Willow Bypass and the Upper Clark Fork River.

The GCTRAN Model

The Groundwater Colloid Transport program GCTRAN was written for this project for use in conjunction with PRZM to account for the special transport characteristics of particles that range from 0.1 to 10.0 μm in size (large-size colloids).

GCTRAN simulates how the mobility of larger colloids will change as the water table fluctuates and as percolating water during floods and heavy rainstorms removes significant portions of the available colloids generated by oxidation processes in the unsaturated zones.

The transport of large colloids as modeled by GCTRAN assumes that these particles are moved with a velocity in the saturated zone that exceeds the average pore water velocity and that these particles have a velocity of zero in the unsaturated zone.

The excess velocity of larger colloids in the saturated zone is based on the assumption that excluded volume effects increase large particle velocities above pore water flow velocities. Excluded volume refers to the portions of the pore water where the average velocity field is small and the diameter of the pores is small. The larger a particle is, the less chance that a particle will pass through the smaller pores during its flow through connected passageways in the open spaces of the soil. The large particle only passes through the pores that have a minimum required diameter and that have higher pore water velocities. Thus the average flow field that the large particle is suspended in exceeds the average flow field velocity of all the soil pores. This increase of the particle velocity to above the average velocity of pore water can be mathematically predicted given a known distribution of pore sizes and assumptions about the pore networks. The differences between average velocities of particles with different sizes in porous matrices is the basis for two commonly used chromatographic separation techniques--size exclusion chromatography and gel permeation chromatography. Size exclusion chromatography has been applied to both polymers in solution and to particles, and gel permeation chromatography is a technique applied to the characterization of polymer mixtures.

NPSOUT treats the larger particles as if they enter the surface water at the same time as runoff and eroded sediment, once they enter the aquifer.

The GCTTRAN program uses a number of parameters to control the way in which large colloids leach into the aquifer. The first parameter is K_d , which predicts a copper metal concentration that corresponds to pH and Eh within a boundary layer of still water surrounding each oxidizing sulfide particle. The parameter PTRANS defines the magnitude of the transport of metal ions to the water outside the boundary layer. In the unsaturated zone outside the boundary layer, the metal ions are assumed to precipitate and then accumulate. When the water table rises, colloids in the risen water are advected by the saturated water flow to the surface water. The parameter controlling water table fluctuation is RIVRIS, a constant that relates cumulative daily rainfall to change in the water table level WATTAB. Daily outflow and a decrement in the water table is assumed to be constant, so that the stream recharge outflow results in a decrement to the water table level RECHDEL, with values ranging from 0.01 to 0.2 cm/day. Using the above hypotheses, transport for large particles and changes in the water table level are predicted for the soil and tailings core.

The Simulation in NPSOUT of Removal of Metals in the Warm Spring Ponds

The section on Warm Springs Pond metal removal efficiency concludes that there is only a limited dependence of metal removal efficiency in the Warm Springs Ponds on flow rate. This apparent limited dependence may be due to the correlation of flow rate with other unknown or unstudied causative factors, such as seasonality and flow history. For this and other reasons discussed later, we used a hypothesis that residence time for the metal in these liming/precipitation ponds does not consistently predict removal, and instead used a constant removal efficiency.

The NPSOUT program removes copper from the stream at the end of Segment 6 of the surface water model (at the exit to Warm Springs Pond 3). The average measured removal efficiency (mass removed/initial contaminant mass) of total copper (suspended and dissolved) between the inlet to Warm Springs Pond 3 and the outlet of Warm Springs Pond 2 is 80.4%. The approach taken for removal of copper metal from the stream in the Warm Springs Ponds was to use NPSOUT to remove 80.4% of all copper loadings from stream loadings to Surface Water Segments 1 through 6.

Sediment-Mediated Transport of Contaminants in Surface Water

Sediment non-point source mass loads are made available through PRZM output. Sediment loadings are provided to the WASP model as a non-point source from the erosion of the stream banks. The characteristics and the quantity of sediment strongly influences transport, removal, storage, and release of heavy metals. The WASP4 Manual (Ambrose et al.) suggests a range for K_d coefficient values from 1.0×10^6 to 6.0×10^3 , with the range depending on the concentration of suspended copper.

Metal distribution and adsorption parameters and sediment/eroded soil particle size distributions are not tabulated for the Upper Clark Fork River, but can be estimated if some simplifying assumptions can be made. For example, K_d varies with season, surface flow, and pH. The ratio of dissolved metal to precipitate and adsorbed metal depends on the extent to which the metal and surface water chemistry has reached equilibrium and on the rate of precipitation. The following estimates predict the ratio of suspended copper metal to dissolved copper metal in the surface waters examined.

(1) A first type of distribution coefficient could be predicted based on conditions in the tailings piles with the assumption that the copper in solution remains in solution in the surface water. If there has been no precipitation, the metals in solution are supersaturated, and if the surface water distribution coefficient K_d remains 234 liter/kg, then the model predicts that the sediment

transports less than 1% (with values generally below 0.25%) of the copper transported. There are other possible values of K_d , depending on the extent of non-equilibrium.

(2) If the distribution coefficient is dependent on the pH and Eh of the surface water a different value must be used. The steps to calculate K_d in surface water are as follows. We initially estimate that copper mass concentration in the suspended stream sediments is 2080 mg/kg, the same as the mine tailings described previously. The soluble fraction can be estimated with pH and Eh, using the program MINTEQA2; if the surface water chemistry includes a pH of 7, Eh of 0.60V, then the soluble copper in surface water equals 3.7 ug/liter. K_d is 5.5×10^5 liter/kg (2080 mg/kg divided by 3.7 ug/liter equals 5.5×10^5 liter/kg).

(3) An alternate number for the copper solids concentration could come from measured flood values described in the RIFR. If a typical suspended copper concentration during a flood is 200 ug/liter, and typical suspended solids concentration for the same flood is 15 mg/liter, then the solids concentration is 200 ug/liter copper/15,000 ug/liter sediment, or 1.33×10^7 ug/kg.

The new surface water K_d is calculated by dividing 1.33×10^7 ug/kg by 3.7 ug dissolved copper/liter (for a value of 3.6×10^6 liter/kg). For such a large value for the ratio of copper in solids to copper in solution, transport by precipitates and sediments would be the predominant copper flux. The large value is a consequence of an apparent enrichment of copper in some suspended river sediments of copper (predominantly in a fine particle fraction). Enrichment of copper in some suspended sediments is consistent with the hypothesis that the surface water carries copper in soluble or colloidal form.

(4) A very different result is obtained if we use the measurements of dissolved copper from the RIFR data sets. K_d can be estimated with dissolved and suspended copper concentrations. Distribution of metal between sediment and solution would vary with chemical conditions and with the amount of suspended sediment. The method for determining surface water K_d using only measured data can be illustrated by the following example.

The following data has been taken from the RIFR. If suspended solids are 20 mg/liter, and suspended copper is 0.2 mg/liter, then the copper solids concentration is 0.2 mg/liter divided by 20 mg/liter, or 10,000 mg/kg. With dissolved copper measured as 0.1 mg/liter, then K_d is 1.0×10^4 mg/kg divided by 0.1 mg/liter, which equals 1.0×10^5 liter/kg.

(5) K_d also may be predicted as varying when pH varies as a function of location or time. pH is not currently predicted within WASP, although the transport of alkalinity, hardness, pH, and related parameters is currently under development. The software to

model variance of K_d with time is also under development. Some spatial variability of K_d is already in WASP.

The adsorption characteristics of the sediment may also play an important part in the transport of metals. Use of the distribution coefficient for precipitation, and the adsorption coefficient for adsorption, are not distinguishable methods, although there is a conceptual difference in the two ways of thinking about metal fate and allocation.

THE WATER QUALITY AND TRANSPORT MODELING PACKAGE

The surface water quality modeling package consists of two separate models, RIVERMOD and WASP4, linked by an interface program.

The River Hydraulics and Sediment Transport Model--RIVERMOD

To simulate the hydraulics of combined Silver Bow Creek/Clark Fork River and their tributaries, a fully implicit river hydrodynamic and sediment transport model (RIVERMOD) was adopted. This model provided the hydraulic parameters for the water quality model WASP4/TOXI4. In the development of RIVERMOD, the Saint Venant equations are used for the conservation of mass and momentum. The sediment transport module uses a sediment yield equation as well as a sediment continuity equation in the sand size range. The hydraulics and sediment transport equations are solved uncoupled, that is, first the Saint Venant equations are solved for hydraulic parameters (Q, Y, V , etc.) and then these are used for the computation of sediment yield and sediment transport from a given segment. Details of this model are given by Hosseinipour (1988a, 1989). In this application, the hydraulic model was modified to include time-variant lateral inflows to better match the flow characteristics of the stream. The sediment transport module was not activated in this project. Natural cross-sectional parameters are provided to the model via a least square equation that relates the flow cross-sectional area as wetted perimeters to water depth in the forms

$$A = a_1 + a_2 y^{a_3} \text{ and } P = b_1 + b_2 y^{b_3}$$

The variables in the above equation are

A = channel flow cross-sectional area

P = wetted perimeter

$a_1, a_2, a_3, b_1, b_2, b_3$ are the parameters obtained using least square procedure for each cross-section.

These are the input to the hydraulic model. A separate code was developed to calculate these parameters for the model.

RIVERMOD can be used to generate quantitative estimates of the bed load (mobile sediment in the stream) and may be used in the

future to predict the suspended sediment that enters the river due to channel and stream bed instability. The alternative to using KENUTIL (which reformats sediment non-point source load from the PRZM time series) is to use the interface from the hydraulics output of RIVERMOD to place the sediment load data in a WASP4 hydraulics reference file.

The Water Quality Model--WASP4

The model readily available for predicting surface water metal concentrations was WASP4/TOXI4. It was developed for sediment and toxic material transport and eutrophication processes in surface water systems, mainly estuaries and wide river basins. The package includes sub-models for hydraulics, eutrophication and toxic constituents. Details of the model are given by Ambrose et al. (1987). In this project, the creek and river from Butte to Deer Lodge was divided into model segments for the use of WASP4.

The primary source of surface water analytical data is the Remedial Investigation Final Report study (RIFR) on the Silver Bow Creek (Tuesday et al., 1987); therefore, the main stream segmentation was chosen to coincide with the measurement stations of that study as outlined in Table 2. Application of the simplified surface water transport model WASP4 results in a metal concentration time series for each surface water segment. The surface water modeling results have been compared to data from the RIFR and from the Montana Water Quality Bureau.

TABLE 2. WASP4 Segments Along the Clark Fork River and Silver Bow Creek

WASP4 segment	Segment length(km)	RIFR Station and location at End of Segment
1	5.0	SS-07 below Colorado Tailings
2	7.9	SS-10 near Silver Bow
3	8.1	SS-14 near Miles Crossing
4	8.0	SS-16 at Gregson Bridge
5	9.9	SS-17 at Stewart Street Bridge
6	5.6	Exit from Warm Springs Pond 3
7	8.1	SS-29 at Perkins Lane Bridge
8	5.0	Between measurement stations
9	8.2	SS-30 near Racetrack
10	8.4	SS-31 Below Dempsey Creek confluence
11	10.6	SS-32 at Deer Lodge

WASP4 was used to predict the surface water quality for the entire stream reach, with 11 segments representing different reaches of the river. Segments 1 to 5 represent Silver Bow Creek. Segments 6 and 7 represent the Warm Springs Ponds or the Mill-Willow Bypass, depending on the volume of the flow. Segments 8 to 11 represent the Upper Clark Fork River.

NPSOUT converts the PRZM unit copper and sediment loading outputs into specific loadings for each segment. The time series from NPSOUT are reformatted as WASP4 reference files. These time-variable and space-variable source terms help determine the surface water contaminant concentrations.

SECTION 6

MINTEQA2 RESULTS

The metal speciation model MINTEQA2 (Brown and Allison, 1987) was used to predict the copper soil/water distribution coefficient K_d for PRZM, which partitions copper between the soil-tailings mixture and the groundwater. This model has been applied to conditions used to describe the tailings piles to determine copper solubility at measured or estimated pH and Eh.

The program MINTEQA2 begins with an initial set of aqueous components and minerals not at equilibrium and then uses equilibrium constants to predict the equilibrium composition of a final solution and the composition of precipitates. Complete specification of the speciation model requires the provision of the appropriate geochemical parameters for each metal complexation and precipitation problem. For our work, the two principal model parameters are Eh (oxidation potential) and pH. Examples of the range of predicted effects of pH and Eh on copper solubility at equilibrium are shown in Table 9.

Eh and pH have been investigated in the unsaturated groundwater at tailings deposit sites along Silver Bow Creek (Figure 7). There is limited data in the RIFR Supplements on Eh and pH in unsaturated zone pore water, in the form of values were measured at several streamside tailings deposits along Silver Bow Creek--Ramsay Flats, the Colorado Tailings, Silver Bow, and the Manganese Stockpile. These sites were extensively studied for the RIFR and have been used as a surrogate for the tailings deposits along the Clark Fork River where no data is available. Some of this data appears contradictory and varies over a wide range, or has been measured by unspecified or questionable experimental methods.

The lowest measured pH value of unsaturated soil pore water was 2.21, taken at between 4 to 6 inches at the Manganese Stockpile simulated rainfall plot (September 23, 1986). The range of pH values for the Manganese Stockpile and the Ramsay Flats simulated rainfall plots between 0 and 6 inches in depth are a pH of 2.21 to 4.01 (at 1-2 inches at Ramsay Flats). The measurement technique is not described in the RIFR Supplement.

The upper measured value of unsaturated soil pH was 6.83, taken at a depth of 6 feet into the pore water sample well site at the Manganese Stockpile (measurement on July 23, 1986). The range of pH values for the pore water sample well sites at the Manganese Stockpile, Silver Bow, and the Ramsay Flats between 4 and 6 feet in depth are a pH of 5.5 (at 4 feet, on October 30, 1986 at the Manganese Stockpile) to a pH of 6.83.

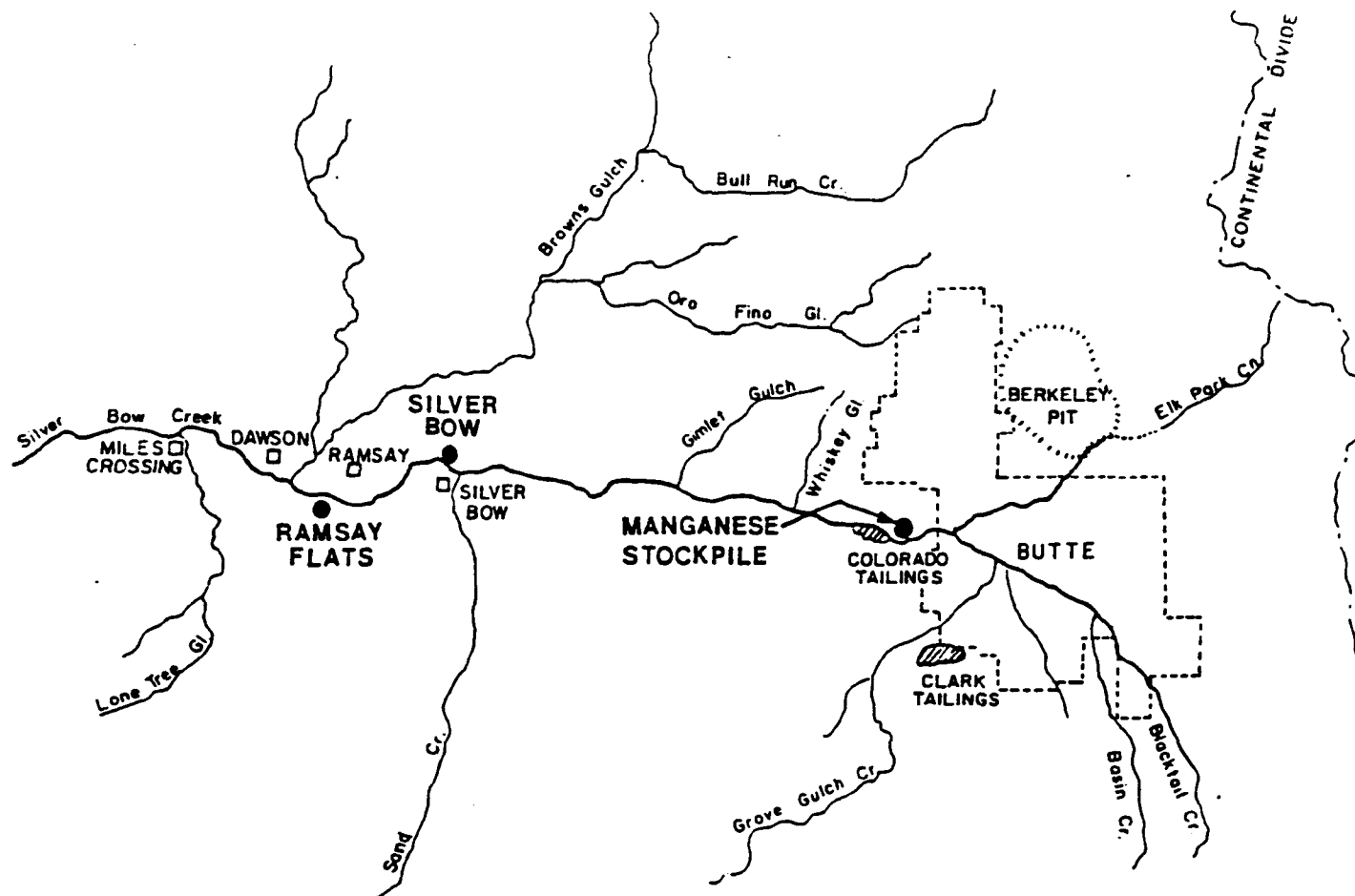


Figure 7. Vadose zone characterization at sites along Silver Bow Creek.

However, for a separate set of measurements of pore water taken at the Manganese Stockpile on April 14, 1986, the result was anomalous pH values of 2.87 to 4.21. These were considered in error since they were outside the range of the previously measured values. These contradictory values and the pH values as a whole provide a possibility to estimate pH values, but not a uniform and certain picture of how pH varies with depth in the unsaturated zone pore water.

These values can be compared to pH for Colorado Tailings in a range of 2.7 to 4.0 at depths of 0.0 to 100 cm. The average pH in fluvially mixed streamside deposits is 4.73 (see RIFR Summary).

Eh measurements were obtained with a platinum electrode measurement. This method of measuring oxidation potential has been judged inaccurate by some inorganic analytic chemists. They argue that the electrochemical couple measured by the platinum electrode is the PtO/Pt redox couple and that the potential measured depends solely on the pH of the solution. The use of a general Eh measurement as a general solution property has been controversial because of the presence of multiple electrochemical couples, each of which may define a separate oxidation potential (see Lindbergh and Runnells, 1984). The uncertainty of the Eh values increases the expected error in Eh and expected error in copper solubility.

However, for the sake of demonstration both MINTEQA2 and a possible first principles approach to predicting the contamination flowing from mine waste dumps, the dependence of Eh and pH on depth was estimated by using extrapolations of measurements within the unsaturated zone in tailings deposits along Silver Bow Creek. Figure 8 shows the influence of soil depth on the median values of pore water Eh measurements from several dates and the unsaturated zone sampling sites. As has been described previously, the measurements of Eh made in pore water in the tailings unsaturated zones were made with a platinum electrode. In order to average the values of Eh in the soil pore water, the two median values of measurements of Eh were determined, and then averaged and plotted in Figure 8. The average values for the Silver Bow site are 344 mV at 4 ft (122 cm) and 60 mV at 6 ft (183 cm). The average values for the Ramsay Flats site are 367 mV at 4 ft (122 cm) and 64 mV at 6 ft (183 cm). Asymptotes for Eh of 450 mV at 0 cm depth and -200 mV at 250 cm depth have been indicated in Figure 8. The median values can be compared to one of the demonstration Eh values, 450 mV. The comparison indicates that the demonstration values for Eh may be at the upper extreme of the actual range of values. If the reader does not wish to regard these values as reliable, then the soil geochemistry profile presented may be considered as primarily illustrative in character.

Eh has been used as a substitute for oxygen concentration in the unsaturated groundwater. Oxygen concentration was tested as a possible parameter in MINTEQA2, but converging numerical solutions did not result when oxygen concentration was fixed. This may be

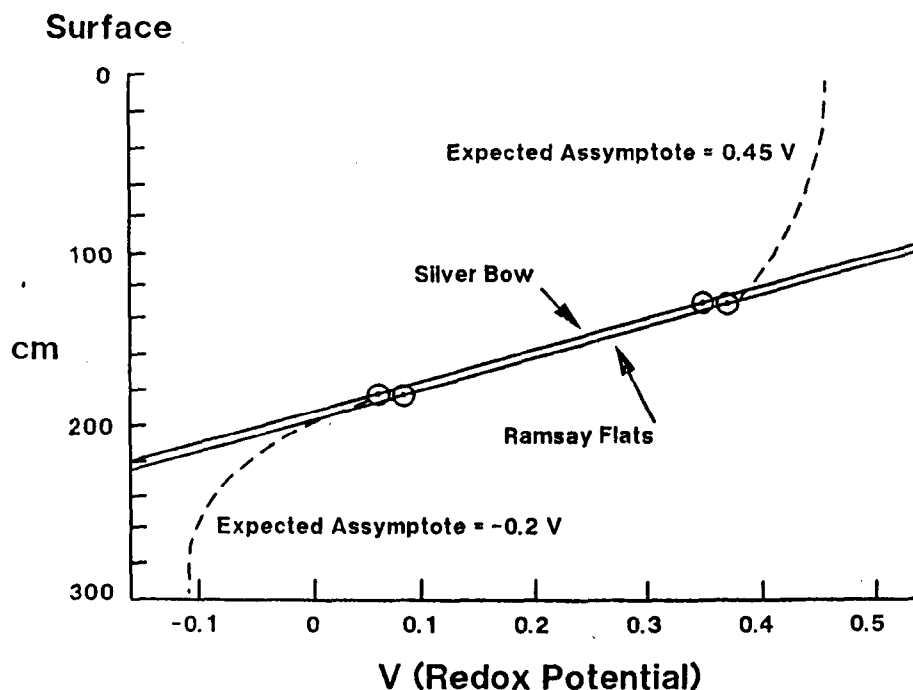


Figure 8. Plot of tailing deposit depth versus oxidation reduction potential (Eh).

because the $\text{H}_2\text{O}/\text{H}^+/\text{O}_2$ electrochemical reduction/oxidation couple, with parameters pH and partial pressure of O_2 , is used by MINTEQA2 to predict Eh, and the resulting Eh is at a sufficiently high value to make difficult the convergence of the MINTEQA2 solution. Consequently, Eh was used directly as an indicator of oxygen concentration.

Table 3 presents a short list of predicted electrochemical potential values for varying pH and the partial pressure of O_2 fixed at 0.21 atmospheres. These results are based upon the $\text{H}_2\text{O}/\text{H}^+/\text{O}_2$ reduction/oxidation couple and the general equation (Krauskopf, 1967).

$$\text{Eh} = 1.23 + 0.0295 \log [\text{ppO}_2]^{1/2} [\text{H}^+]^2$$

Table 3. Eh versus pH for a
Fixed Oxygen Content of
0.21 Atmospheres

pH	Eh (mV)
2.5	1070
3.0	1040
4.0	980
5.0	930
7.0	800
7.5	770

Table 4 presents predicted electrochemical potential values for pH = 7.0 and an oxygen partial pressure that varies from 0.21 atmospheres to 0.0001 atmospheres. These results are also based upon the $\text{H}_2\text{O}/\text{H}^+/\text{O}_2$ reduction/oxidation couple.

Table 4. Eh Versus Oxygen Content
for a Fixed pH of 7.0

O_2 partial pressure (atmospheres)	Eh (mV)
0.21	800
0.002	770
0.0001	750

The apparent limited variance of Eh when the partial pressure of O_2 is reduced to below its probable range for even soils below 200 cm indicates that the $\text{H}_2\text{O}/\text{H}^+/\text{O}_2$ reduction/oxidation couple does not predict the behavior of reduced geochemical environments. An optimal expected range of Eh for oxidizing conditions would be between 450 mV and 800 mV. 450 mV and 600 mV are representative values for Eh in some of the predictions about the solubility and mobility of heavy metals in oxidizing conditions made using MINTEQA2.

The soil and tailings core has been divided as described in Table 5 to represent the idealized soil core geochemistry and because PRZM solves for transport through multiple soil layers. Depths of the various layers have been based on unsaturated zone

data from the tailing deposits along Silver Bow Creek and on sulfide/sulfate profiles at the tailing deposits at Anaconda (Tetra Tech). Descriptions of increased sulfide content with increasing depth in tailings and smelter waste impoundments are available in the Tetra Tech report on the Anaconda Smelter site (Tetra Tech, 1985).

Sulfide/sulfate ratio profiles are provided in the Anaconda Smelter report, for tailings deposits that are above the water table. The sulfide/sulfate profiles are provided in the Anaconda report as a guide to the soil geochemistry profile. The ratio of sulfur in sulfide form to sulfur in sulfate form decreases as the depth of the tailings decreases and as the age of the deposit increases. Each range of sulfide/sulfate ratios represents a separate soil care layer.

Sampling well sites TS-14 and TS-16 were used as representatives of the streamside tailings unsaturated zone geochemistries because these are the two unsaturated soil sampling wells closest to the Silver Bow Creek at the Ramsay Flats sampling area.

TABLE 5. Demonstration of Soil/Tailings Strata and Geochemistry

Tailings layer	Depth (cm)	pH	Eh (mV)
Oxidation layer	0-100	3.0-5.0	450-800
Intermediate layer	100-150	5.0	450
Mixing layer	150-200	7.0	450
Reducing layer	>200	7.5	-200

If we use the idealization that the tailings deposits have a uniform composition and porosity, we would expect the structure of the deposit geochemical profile to be uniform, with similar oxygen consumption rates and similar oxygen diffusion and advection rates. The groundwater depth should not affect oxygen transport in the unsaturated zone.

Advection of oxygen into the unsaturated zone when saturated groundwater levels rise during river bank storage might be an important exception. For such a case, oxygen would enter from below as well as from above the unsaturated zone. For the Anaconda site, the ground water is much further from bank storage of the river and should have much less oxygen dissolved in the groundwater aquifer.

Iron, copper, arsenic, lead, cadmium, and zinc have been included in excess of actual groundwater concentrations in order to allow MINTEQA2 to calculate saturated solutions for each of these

heavy metal contaminants. The metal transport predictions will emphasize copper transport. The system of models can be used on other metals such as cadmium, zinc or arsenic.

The ligands in solution in the unsaturated zone groundwater are included in the MINTEQA2 input file, based upon the vadose zone groundwater composition measurements. Analytic data on unsaturated groundwater in tailings deposits was used for Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , and F^- . Ca^{2+} is included in excess to assure a saturated solution. Fluoride and chloride (F^- , Cl^-) anions are included with the soluble fraction the same as the input fraction because there is no fluoride or chloride precipitation.

Sulfate (SO_4^{2-}) has been included at large concentrations (0.03 m/liter) because of the presence of sulfides in the tailings and waste rock, and because the resulting concentrations are close to actual saturated zone concentrations of 0.025 m/liter. Carbonate (CO_3^{2-}) has been set using CO_2 partial pressure at the atmospheric value of 3.3×10^{-4} atmospheres in order to replicate the minimum of the expected large carbonate concentrations from the abundance of calcareous bedrock and alluvia in the Butte and Upper Clark Fork River basin. An expectation of larger carbonate concentrations would lead to the fixing of a larger CO_2 partial pressure - refinements of this demonstration may show that a larger fixed CO_2 partial pressure is more appropriate.

Larger organic ligands are assumed not to be present; surface water analytical data indicate this is true, although analytical data on soluble organic ligands are not available for the vadose zone.

The solid phases present may be determined in advance by reasonable guesses as to metal and sulfur oxidation states and by the saturation indices for minerals provided at the end of our initial MINTEQA2 model runs. Solid species that form under the conditions in the top 100 cm include gypsum (CaSO_4), goethite (FeOOH), hematite (Fe_2O_3), cuprous ferrite ($\text{Fe}_2\text{Cu}_2\text{O}_4$), anglesite (PbSO_4), franklinite (ZnFe_2O_4), and cadmium arsenate (CdAsO_4). The above minerals are predicted to precipitate because they are thermodynamically optimal; nevertheless, the probability that some of these minerals will form is small. For example, while hematite is the thermodynamically optimal iron oxide, the probable precipitate from a solution at ambient temperature and pressure will be goethite or an amorphous iron oxide. Hematite is geologically unlikely to form, although a mineral with a different crystalline structure but the same stoichiometry may be formed.

Cupric ferrite (CuFe_2O_4) is not the thermodynamically favored copper oxide precipitate for the above conditions. MINTEQA2 predicts precipitation of cuprous ferrite as the primary copper mineral in the oxidized zone. This result is dependent not only on

TABLE 6. Non-precipitating Component Concentrations in the Unsaturated Zone Pore Water of the Tailings Deposits (at Sampling Well TS-16) and Precipitating Components in Excess of Measured Concentrations

Component	Component concentration before precipitation (m/liter)
Mg ²⁺	1.28 x 10 ⁻²
Na ⁺	1.09 x 10 ⁻²
SO ₄ ²⁻	0.03
F ⁻	1.0 x 10 ⁻⁴
Cl ⁻	1.3 x 10 ⁻³
Ca ²⁺	9.1 x 10 ⁻³
CO ₃ ²⁻	4.9 x 10 ⁻⁴
Cu ²⁺	0.001
Zn ²⁺	0.001
Fe ²⁺	0.006
H ₃ AsO ₃	0.0001
Pb ²⁺	0.0001
Cd ²⁺	0.0001

the geochemical conditions but on the assumptions or estimates of K_{sp} for the precipitates, especially for cuprous ferrite. The value for $-\log (K_{sp})$ in the MINTEQA2 thermodynamic data base of MINTEQA2 is 8.92. This estimate is experimentally determined, and other measurements may produce different solubilities; variance in K_{sp} will affect the amount of copper predicted to be in solution. For example, if $-\log (K_{sp})$ is 6.77 then $[Cu^{2+}]$ will be increased, possibly by as much as two orders of magnitude.

The results indicate that many species will be highly transportable for moderate to very acidic pH and for oxidizing Eh. From the most mobile, as detailed in Table 7, to the least mobile, the hazardous heavy metals are arsenic, cadmium, zinc, copper, lead, and iron. In Table 8, the MINTEQA2-predicted soluble copper fractions are provided, along with the calculated partition coefficient, based upon a typical solids composition of 2.08 g copper/kg mixed tailings.

The method for calculation of K_d is to divide the total copper in 1 kg of soil/tailings by the mass of total soluble copper in 1 liter of water. For example, for 2.08 g/kg Cu in the solid mass of 1 kg, there is (molecular weight of Cu, g/m) $63.5 \times$ total Cu in solution (in moles per liter) in 1 liter of groundwater. For total

TABLE 7. Species Formed for pH=3.0,
Eh=600mV

Species formed	Concentration (m/liter)
Cu^{2+}	3.8×10^{-4}
Cu^+	6.5×10^{-12}
Zn^{2+}	1.0×10^{-3}
Pb^{2+}	1.5×10^{-5}
H_3AsO_3	1.6×10^{-12}
H_3AsO_4	1.0×10^{-4}
Cd^{2+}	1.0×10^{-4}
Ca^{2+}	7.3×10^{-3}
Mg^{2+}	1.3×10^{-2}
Na^+	1.1×10^{-2}
Fe^{2+}	8.2×10^{-7}
Fe^{3+}	1.1×10^{-7}
SO_4^{2-}	2.8×10^{-2}
Cl^-	1.3×10^{-3}
F^-	1.0×10^{-4}
CO_3^{2-}	1.2×10^{-5}

Cu in solution of 3.8×10^{-4} m/liter, the result is K_d of 2.08 g/kg / 2.4×10^{-3} g/liter = 86.

Table 8 and Table 9 present values for the copper K_d predicted by MINTEQA2 for idealized representations of geochemical conditions in mine tailings piles and stream side deposits.

TABLE 8. Calculation of K_d from Mass Fractions, for Eh = 450 mV

Core layer	Copper fraction in solid phase (m/kg)	Copper fraction in liquid phase (m/liter)	K_d (m/kg / m/liter)
Oxidation layer	0.033	1.04×10^{-6}	31496
Intermediate Mixing layer	0.033	1.08×10^{-8}	3.3×10^6
Mixing layer 1.85×10^8	0.033	1.77×10^{-10}	

TABLE 9. Copper K_d and Dependence on pH and Eh

K_d	Soil Core Layer	pH	Eh (v)
4.3×10^{15}	Reducing	7.0	-0.2
1.85×10^8	Mixing	7.0	0.45
5.5×10^5	Mixing	7.0	0.60
3,300,00	Intermediate	5.0	0.45
	Mixing		
8,850	Intermediate	5.0	0.60
	Mixing		
31,496	Oxidation	3.0	0.45
86	Oxidation	3.0	0.60

For the case of copper solubility, the approximate effect of raising pH by 1.0 is to lower solubility by $\times 0.1$, and the approximate effect of raising Eh by 150 mV is to increase solubility by $\times 400$.

The results shown in Table 9 indicate that, for an Eh range from 450 mV to 600 mV, and a pH range from 3.0 to 5.0, the oxidation layer has a range of K_d from 86.2 to 3,300,000. All of our calibrated K_d values fall in the lower portion of this range.

A caution should be applied to the use of uncalibrated distribution coefficients that rest solely upon equilibrium predictions. The model presented here assumes that precipitation occurs to the full extent that is predicted by the equilibrium case. The kinetic limit on the rate of precipitation of goethite (or other ferric hydroxides, both amorphous and crystalline) and the rate of precipitation of cuprous ferrite may be of sufficient significance to caution against reliance on K_d predictions that are outside the ranges of calibrated values.

SECTION 7

PRZM CALIBRATION

PRZM predictions include contaminant transport and ground surface water flow. The flow predictions were calibrated first: the differences between the predicted flow and the measured flow in an experiment represented the quantity to be minimized by calibration.

The sources of data for the model application included the Silver Bow Creek Remedial Investigation Final Report, National Oceanic and Atmospheric Administration (NOAA) meteorological data, and US Geological Survey reports and data on stream flow. Meteorological data in the form of daily maximum and minimum temperature and daily precipitation have been assembled from tapes sent to ERL-Athens from NOAA's Climatic Data Center. Topographic data from maps provided by Superfund site managers were used to establish stream and river bed perimeters, slopes and slope lengths. The surface features of the stream banks were used to make initial estimates of the area of leaching from the unsaturated soil and tailings strata into the saturated groundwater.

GROUND SURFACE HYDROLOGY DATA

Parameters for modeling use may be uncertain or may only be known to be within a range of values. In order to calibrate the water flow model (linked here with the mass-transport model), PRZM must be run with a range of values for important parameters. To calibrate parameters that affect predictions, empirical data and site data should be considered.

Application of the program PRZM requires ground surface and subsurface hydrologic data for the Upper Clark Fork River subsites. Ground surface hydrology describes the overland flow to Silver Bow Creek and the Clark Fork River from surrounding hillocks, stream banks, and plains. Slope and slope length are parameters for the Universal Soil Loss method and are incorporated into PRZM. PRZM also requires hydrologic parameters for the SCS Curve Number method and for water balance calculations.

Soil and waste deposit properties (such as composition and hydrology) vary over the entire Silver Bow Creek Superfund site. In order to represent this heterogeneity, the Silver Bow Creek site has been partitioned into subsites, each of which requires specific site data.

Current data are available primarily for the Silver Bow Creek streambank tailings deposits. Data from Silver Bow Creek have been used to represent the entire Superfund site up to Deer Lodge. We

assumed that the streamside deposits of mining waste above the Warm Springs Ponds are similar to those below the Ponds.

Tailings data on Silver Bow Creek drilling sites include depth of water table, pH, composition (clay, sand, silt, rock) and aqueous and solid geochemistry. Drilling site data were chosen based upon the level of soluble contamination. The 11 sites that had the highest soluble (oxidized) copper composition in any layer were used for tailings data. These sites are in the process of releasing metals. The sites resemble the original high sulfide ores at the buried depths and will have a lower sulfide content at the surface. This demonstrates that some aging and weathering of the mining waste has occurred.

The sites that were not chosen as representative had extensive fresh pyritic sulfur near the waste deposit surface. Such sites are not yet oxidized sufficiently to be modeled using a transport and solubility-limited model. A more appropriate model for fresh tailings and waste would be a source term that increases over time to approach the value of the weathered waste source term (with kinetic limitations on metal oxidation product fluxes). The unoxidized sites are unsteady increasing sources that have lower magnitude metals fluxes than the sites we have included.

The options for representation of water content, wilting point, and field capacity are to have the model calculate from soil/tailings makeup or to use correlations. The PRZM model will calculate bulk density, wilting point, and field capacity from composition data. Both having the program calculate the input variables and doing the calculations by hand were tried. The method chosen was to let the program calculate the values. In this way, calibration to fundamental composition variables is possible.

Table 10 indicates the parameters to be calibrated, their ranges of values, and the site characteristics represented by those values.

CALIBRATION METHODOLOGY

For a set of deviations of predictions from a set of measurements, the distribution of deviation magnitude depends on parameters chosen; calibration consists of minimizing some statistical function of this set of deviations. The most logical function to be minimized to a uniform value is the standard deviation for relative variations in parameters, so that the magnitude of result variance is uniform for the same relative change in all parameters.

Each parameter in the input file has a functional contribution to the predicted result. Variables with smaller effects can be left out of the calibration process because their

TABLE 10. Hydrologic Parameters for Water Flow and Mass Transport to be Included in PRZM

Parameter	Value (units)	Description
SCS curve number	58	Meadow, Type B soil
SCS curve number	89	Rangeland, Type D soil (poor condition, impermeable soil)
SCS curve number	90	Type D soil
Sand content	45.1%	
Clay content	11.8%	
Grade (slope)	2.0%	Slope of Colorado Tailings
Slope length	100 feet	
USLE LS parameter	1.7	Determined by slope and grade
USLE K parameter	0.42	Soil erodability factor, for fine sand and <0.5% organic matter
Hydraulic drainage rate	1 day ⁻¹	Free draining field, totally drained to field capacity in 1 day
Hydraulic draining Drainage Rate loam	1.6 day ⁻¹	R e s t r i c t e d field, for clay
Field capacity	0.232 cm water/ cm soil	Water content at -0.33 millibar capillary pressure
Initial water content	0.232 cm water/ cm soil	
Wilting point	0.057 cm water/ cm soil	Water content at -15.0 millibar capillary pressure

large relative variations result in a minimized standard deviation. Instead, what has been done is to vary parameters that will change the prediction changes by a relatively large percentage with a small percentage change in the variable value. For such a parameter, standard deviation from measured values will be large for all ranges of the large effect parameter except for the range about the value that minimizes the difference between prediction and the measured value. This approach calibrates the model to the variables to which it is most sensitive.

There is a subset of model parameters that have a significant effect on the ratio of runoff to infiltration. Other parameters are kept constant during the calibration and as close as possible to the known values for typical sites along the river. Application of PRZM (Table 11) shows the parameters to which the predictions are most sensitive and indicates the parameters that can most efficiently minimize the difference between predicted runoff and measured runoff.

TABLE 11. Initial Calibration Parameters Grid for 2.44-cm Storm Precipitation

Sand content	Clay content	Hydraulic drainage rate	SCS curve number	Infiltration (cm)
20%	8%	Free drainage	58	2.44
60%	8%	Free drainage	58	2.44
20%	18%	Free Drainage	58	2.44
60%	18%	Free drainage	58	
20%	8%	1.6 day ⁻¹	58	2.44
60%	8%	1.6 day ⁻¹	58	
20%	18%	1.6 day ⁻¹	58	
60%	18%	1.6 day ⁻¹	58	
20%	8%	Free drainage	86	1.71
60%	8%	Free drainage	86	
20%	18%	Free drainage	86	
60%	18%	Free drainage	86	
20%	8%	1.6 day ⁻¹	86	1.652
60%	8%	1.6 day ⁻¹	86	1.646
20%	18%	1.6 day ⁻¹	86	
60%	18%	1.6 day ⁻¹	86	1.76

As can be seen from this grid of parameters and the infiltration results (Table 12), the sensitivity in the model to these parameters is (in order of decreasing sensitivity): the SCS curve number, the clay and sand content, and the drainage rate .

TABLE 12. Sensitivity of PRZM
Parameters and Results

Variable	Sensitivity ^a
SCS CN	-0.669
Clay content	0.055
Drainage	0.034
Sand content	-0.002

^aAbsolute change in infiltration/absolute change in variable

The best estimate of the parameters to which the model results are less sensitive were used for the final calibration. For example, the value initially used for drainage rate was 1.6 /day, the value for clay loam, although it was later set to the Free Drainage option of 1.0 day⁻¹. The values used for clay and sand content were the median values for the tailings sites chosen from the drilled and sampled sites recorded in the Remedial Investigation Final Report (Appendix B, Part 3) and identified in the report chapter on site geochemistry and metal speciation data (45.1% sand, 11.8% clay). Other general numbers for tailings composition have been produced. The Colorado Tailings have an approximate composition of 90% sand. The fluvially mixed streamside deposits between Butte and Deer Lodge have an average composition of 55% sand and 10% clay (see RIFR Summary).

RUNOFF AND INFILTRATION CALIBRATION

To determine the water infiltration parameters, PRZM results are compared with a results from simulation of rainfall, infiltration, and runoff at two sites on the banks of Silver Bow Creek (Figure 9). These simulated rainfall tests were conducted at the Ramsay Flats and the Manganese Stockpile (see Supplemental RIFR, Appendix C).

The simulated rainfall rates applied to the test plots were 0.2 in/hr, 0.8 in/hr, and 2.0 in/hr. The simulated rainfall was applied for 1/2 hour. The test dates were September 23 to 26, 1986. Runoff volumes from the plots were measured and infiltration volumes were calculated as applied simulated rainfall minus runoff volume.

The following ratios of infiltration to total precipitation have been calculated from measured runoff volumes on the site for

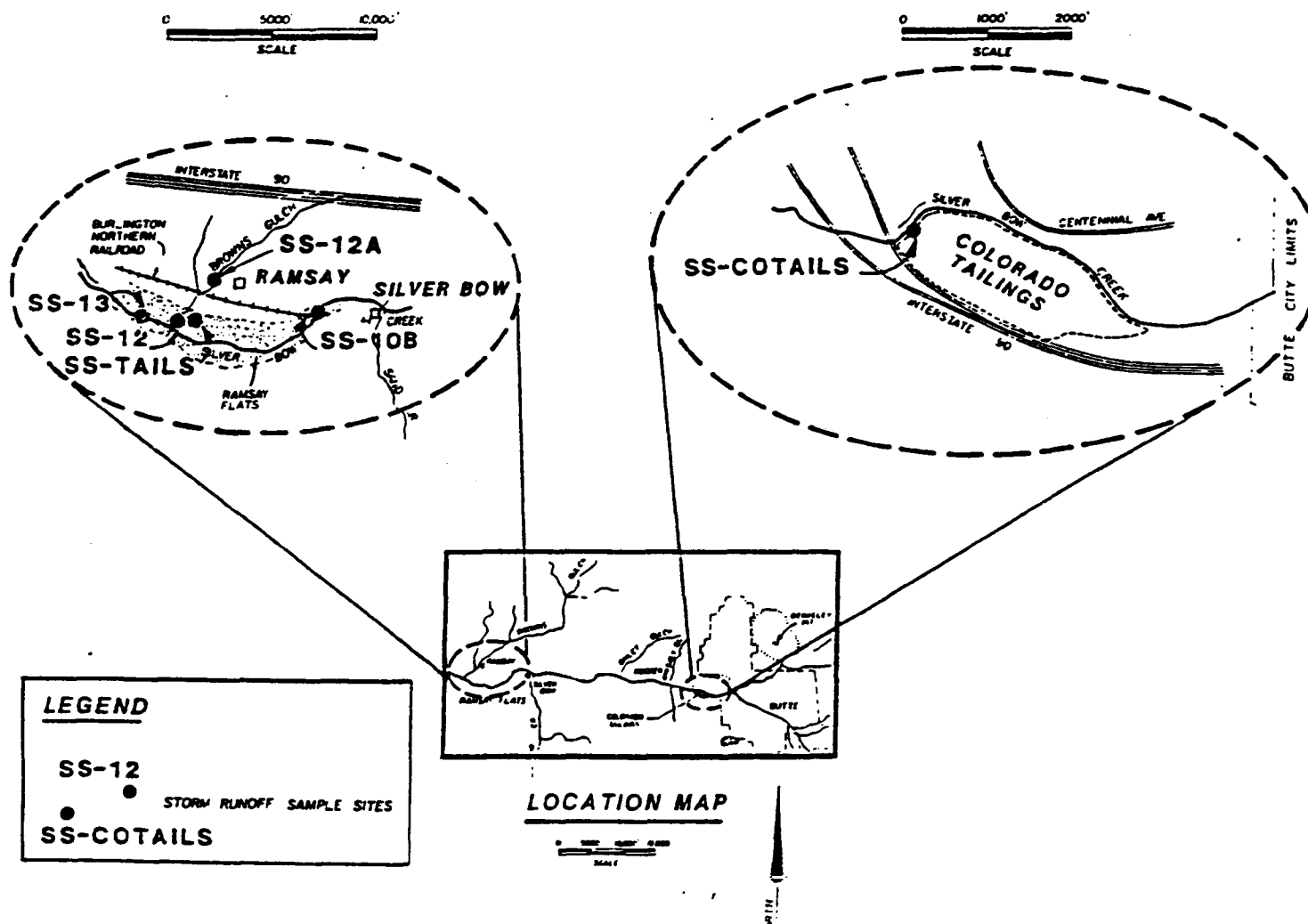


Figure 9. Storm runoff sampling sites at Silver Bow Creek.

1/2 hour tests (Table 13). The rates of infiltration were extrapolated to hypothetical rain storms of 4.5 hours in duration. These estimated (from measurement) infiltration volumes during rain storms were compared with the predictions of total infiltration from rain storms with the same total precipitation that have been modeled by PRZM. The volume for such a storm is included into the meteorological data for September 1986 used as input data to a PRZM run.

TABLE 13. Simulated Rainfall

Site	Application rate (extrapolated rainfall)		
	0.2 in/hr (2.29 cm)	0.8 in/hr (9.14 cm)	2.0 in/hr (22.9 cm)
Manganese Stockpile			
Infiltration ratio	0.225	0.210	0 . 2 4 3
Extrapolated Total infiltration	0.514 cm	1.92 cm	5.56cm
Ramsay Flats Site			
Infiltration ratio	0.238	0.251	0.113
Extrapolated Total infiltration	0.545 cm	2.30 cm	2.59 cm

THE EFFECT OF ANTECEDENT MOISTURE

The moisture present in the soil before precipitation, also known as the antecedent moisture condition, can affect the infiltration predicted by the SCS Curve Number method. It is important to know if the same plot of land was used for sequential experiments or trials, as this would affect the antecedent moisture conditions, and should lead to an adjustment in the meteorological data used for the calibration.

The conditions under which the experiment was performed are not known. To determine if the antecedent moisture condition affected the measured runoff and should be taken into account during calibration, PRZM was tested for sensitivity to two types of antecedent moisture conditions. The conditions used in the PRZM input files reflected the field conditions. For example, the PRZM input files used the same date as the runoff experiment and local meteorological data. The PRZM results illustrate how total infiltration reaches a minimum as antecedent moisture is increased. This result is consistent with PRZM's use of the SCS Curve Number equations to predict infiltration and runoff.

The first type of antecedent moisture condition tested is an increase in initial soil moisture content. With a storm event of 2.29 cm, the initial soil moisture content of 0.232 cm/cm was large enough to reduce infiltration to a minimum value, as is shown in Table 14.

TABLE 14. Antecedent Moisture Conditions: Fixed Initial Water Content

Fixed initial water content (cm/cm)	Infiltration (cm)
0.232	1.21
0.45	1.21

For the second type of antecedent moisture condition, where regular rainfall occurs with a fixed rate for the week before the rainstorm, the amount of infiltration also reaches a minimum as the antecedent rainfall rate increases.

TABLE 15. Antecedent Moisture Conditions: Fixed Rainfall for the Previous Week

Rainfall rate (cm/day)	Infiltration (cm)
0.1	1.47
0.3	1.21
1.0	1.21
3.0	1.21

The sensitivity results from Tables 14 and 15 indicate that the antecedent moisture condition can be set at a reasonable value such as field capacity (0.232 cm/cm). If there is a dry soil condition or minimal rainfall preceding the storm event, then the infiltration will be underestimated by PRZM. For the date examined (September 23-26, 1986), the previous week of rainfall did not

exceed an average of 0.1 cm/day. For this reason, the estimate of curve number based on the PRZM calibration runs may be sensitive to any real cases where the initial soil moisture content is less than 0.232 cm/cm.

RUNOFF CALIBRATION RESULTS

Table 16 shows that for an initial calibration to a 2.29 cm storm rainfall in 4.5 hours (refer to Table 11), total infiltration should range between 0.514 and 0.545 cm. An SCS curve number of 97 predicts infiltration near the two measured values of 0.514 cm and 0.545 cm infiltration.

TABLE 16. SCS Curve Number
Versus Infiltration for 2.29
cm Storm Precipitation

SCS curve number	Infiltration (cm)
90	1.297
94	1.00
97	0.59
99	0.28

Table 17 shows the final calibration to a storm rainfall of 9.14 cm. For a storm rainfall of 9.14 cm, the expected infiltration (see Table 13) should vary between 1.92 and 2.30 cm. A curve number of 90 predicts infiltration of 1.96 cm (within the expected range).

A curve number calibrated to a storm rainfall of 9.14 cm, should predict values of infiltration that deviate from the measured values for the 2.29 and 22.9 cm storm volumes. For example, the expected infiltration for 2.29 cm of rainfall is 0.514 cm to 0.693 cm but the predicted infiltration with Curve Number equal to 90 is 1.3 cm. For a storm rainfall of 22.9 cm, the predicted infiltration with Curve Number equal to 90 is less than the actual infiltration of 2.59 cm to 5.56 cm.

EROSION CALIBRATION

Following the calibration of runoff and infiltration from a typical site on the river bank, the surface erosion of soil and the PRZM input parameters must be calibrated using the relation of the predicted erosion to known erosion.

TABLE 17. SCS Curve Number
Versus Infiltration for
9.14 cm Storm Precipitation

SCS curve number	Infiltration (cm)
89	2.9
90	1.96
94	1.35
97	0.70

Erosion data are not available for the Clark Fork River. Instead, reference is made to a storm that is accompanied by Silver Bow Creek tributary flow and total suspended solids data. The storm of May 29, 1985, had 0.97 cm of precipitation. Suspended solids content in the runoff for several tributaries to the Metro Storm Drain and Silver Bow Creek from specific drainage watersheds above and around the Butte mines was measured.

Table 18 provides the May 29, 1985, suspended solids data for each measuring station. Each measuring station was placed below a watershed with a known surface area.

The tributary flows that correspond to these erosion data can be predicted using PRZM and the parameters calibrated above, or can be taken from flow composite data (unpublished RIFR data). The use of two different flow rates for the tributaries leads to two different calibrations, but the most reliable calibration is believed to be based on the PRZM runoff predictions.

TABLE 18. Total Suspended Solids
for May 29, 1985, Storm

Measuring station	Total suspended solids (mg/liter)	Eroded mass (tonnes/ hectare)
PS-01	1890	0.0266
PS-02	1440	0.0203
PS-04	2650	0.0373
SS-02	272	0.0038

The erosion parameters varied for the calibration are the Universal Soil Loss Equation Length of Slope parameter (USLE LS) and the Universal Soil Loss Equation erodability parameter (USLE K). The SCS method management practice parameters P and C do not apply, because the sites are uncultivated. The USLE K parameter ranges from 0.05 (sand, <.5% organic content) to 0.38 (loam, <.5% organic content). The USLE LS parameter ranges from 0.07 (0.5% slope, 25 ft length) to 0.18 (1% slope, 300 ft length).

EROSION CALIBRATION USING FLOW BASED ON RUNOFF PARAMETERS

To use the measured total suspended solids we must determine how many liters of runoff occurred for that day. Using PRZM variables from the previous calibration of runoff, runoff per hectare at 0.141 cm for May 29, 1985, is predicted by PRZM using 1984-1985 meteorological data. This volume is 1.41×10^{17} cm³/hectare.

By conversion, this value is equivalent to 0.447 ft³/sec for a watershed area of 77.8 hectares. The measured area of the watershed for PS-04 is included in Table 19 and was measured from a map using a planimeter. For 2650 mg/liter of total suspended sediment, conversion to total eroded sediment for the 0.447 ft³/sec flow from 77.8 hectares shows a predicted total eroded mass of 2.9 tonnes or 0.0373 tonnes/hectare for this one day (see Table 18).

The ratio of erosion per hectare to total suspended solids for May 29, 1985 with fixed runoff versus infiltration parameters is 0.0373 tonnes/hectare for 2650 per mg/liter of suspended solids (see Table 18).

TABLE 19. Erosion Parameter Calibration
Grid for 0.97-cm Storm Precipitation

USLEK	USLELS	Erosion (tonnes/hectare)
0.38	0.18	0.0373
0.38	0.07	0.0353
0.05	0.07	0.0046
0.25	0.18	0.0601
0.24	0.10	0.0318
0.12	0.07	0.0111
0.18	0.09	0.0215

The measured value of eroded sediment per liter to be used is an average of the two central values for total suspended solids, 1440 and 1890 mg/liter, and eroded sediment per day of between

0.0203 and 0.0266 tonnes/hectare. An average rate of suspended solids eroded from the land surface for this event is 0.0235 tonnes/hectare-day.

The calibration of the erosion parameters USLEK and USLELS is as follows. The best fit value for USLEK (0.18) represents half loamy sand and half loamy fine sand. The value for USLELS (0.09) represents a slope of 0.5% and slope length of 75 ft. An erosion rate of 0.0215 tonnes/hectare results for the calibration date, May 29, 1985.

CALIBRATION OF EROSION BASED UPON FLOW COMPOSITE DATA

Runoff volumes from the eroded Butte sites can be determined from either the PRZM model as was done above or by the Flow Composite method followed by the authors of the Remedial Investigation Final Report. Flow/surface runoff data for May 29, 1985 were gathered by the Flow Composite method. Flow composite data uses total flows during the 90-minute storm hydrograph, and then calculates the average flow during the storm.

Runoff in Table 20 was derived from conversion of acre-ft to hectare-cm using the watershed areas calculated with a planimeter from the map of the Silver Bow Creek Watershed that accompanied the erosion study section of the Remedial Investigation Final Report. The average value of the two central runoff depths for the storm is 0.231 cm. This value can be compared with 0.141 cm of runoff for May 29, 1985, as predicted by PRZM.

TABLE 20. Flow Composite Data for May 29, 1985, Storm

Measuring station for watershed	Surface area (hectares)	Flow (acre-ft)	Runoff (cm/hectare)
PS-01	31.2	0.25	0.099
PS-02	77.5	2.28	0.363
PS-04	77.8	3.96	0.628
SS-02	87.7	0.38	0.0535

More runoff coincides with more erosion because the basis of our erosion estimates is the data available on suspended sediment per liter. The average measurement of erosion per hectare (from a

PRZM-generated runoff of 0.141 cm) at 0.0235 tonnes/hectare can be compared with an erosion per hectare (for the Flow Composite measure runoff data of 0.231 cm) at 0.0385 tonnes/hectare.

The Flow Composite data predict more erosive parameters than the PRZM prediction runoff data. The Flow Composite data fit best to erosion parameters that have the following values. The best fit value for USLEK (0.38) represents loam. The value for USLELS (0.18) represents a slope of 1% and slope length of 300 ft. These erosive parameters predict more erosion (0.0373 tonnes/hectare on the calibration date, May 29, 1985) than the values calibrated to the PRZM runoff results. Nonetheless, the erosion parameters calibrated to PRZM runoff have been used.

SECTION 8

MINING WASTE MASS ESTIMATES

The variability of the off-stream sources over a year implies that there are both seasonal sources and permanent sources. The seasonal sources include the off-stream subsites in Butte and at the Anaconda Smelter (see Table 1). The sub-surface drainages from underground mine networks and mine pits in Butte constitute a permanent set of drainage sources that are represented in NPSOUT as having no seasonal variance.

PHYSICAL STRUCTURE OF THE BUTTE MINES DUMP SITES

The dump sites in the Butte vicinity total 2592 acres or 1049 hectares, based upon the estimates available from the soils screening study work plan. The adjustment factor in NPSOUT used to correct the area of this tailing deposits site is B (for Butte). The adjustment factor B can be considered a correction for data errors in the area estimates. B also can be considered an adjustment for differences in the contaminant source characteristics of the off-river waste deposits versus the on-river streamside tailings deposits.

The Butte subsite is primarily composed of 1750 acres of waste rock dumps and 750 acres of the Yankee Doodle tailings. If this Butte subsite area estimate is correct, then the adjustment factor B should be 1.0. Future work in application of this model should include examination of the physical structure of these dumps and evaluation of the dump site areas using aerial photographs. The final value of B settled on and used is 1.0 .

PHYSICAL STRUCTURE OF THE ANACONDA DUMP SUBSITES

In the Tetra Tech RIFR for Anaconda, the Anaconda Opportunity Ponds are estimated to be 6000 acres (2429 hectares) in area and to have an estimated waste mass of 2.5×10^8 tons.

The use of this area in predicting the magnitude of the off-river metal source loadings requires an adjustment parameter in NPSOUT, A (for Anaconda), and a set of peak loadings from the off-river sources.

To have the correct proportionality between the metals entering the Clark Fork from Warm Springs Creek (considered to be the entire loading from Anaconda) and metals from the Opportunity Ponds seepage drains, German Gulch, Brown's Gulch, and Mill-Willow

Creek, the metal fluxes for May 7, 1985, (a peak Cu loading date in our data) were used (Table 21). The correction factor **A** is applied to 6284 kg/day of peak loadings from the Anaconda subsite, and corrects the subsite area to 1500 hectares when $A=0.24$. Using calibration to determine the magnitude of **A** is an important step. Future work will include examination of the physical structure of these dumps and evaluation of area from aerial photographs. The final calibrated value of **A** used is 0.24 .

TABLE 21. Peak Copper Fluxes into the Clark Fork Basin
May 7, 1985, RIFR Measurement

Source	Station	TOXI4 Load	Dump site
Brown's Gulch	SS-12	145	tailings
German Gulch	SS-15	170	tailings
Opportunity Ponds	SS-23,24	46	treatment ponds
Mill-Willow Creek	SS-18	1401	tailings and seepages
Warm Springs Creek	SS-28	6284	Anaconda smelter waste

MINE DRAINAGE FROM THE BUTTE MINES

One important source of Cu into Silver Bow Creek above the RIFR Measuring Station SS-07 is an underground mine-shaft network under the Butte area that drains at an approximately constant rate into the Metro Storm Drain and other storm drains and empties directly into Silver Bow Creek. This source plus variable sources on the same site result in a 2800 kg/yr to 4100 kg/yr loading of Cu into Silver Bow Creek. The mine drainage carries copper into Silver Bow Creek at an estimated rate of 2373 kg/yr (6.5 kg/day).

PHYSICAL DIMENSIONS OF THE STREAMSIDE TAILINGS DEPOSITS

The area covered by the tailings along the banks of the Clark Fork River has been determined using a set of maps prepared from aerial photographs that have been converted to show vegetation type and extent of vegetation cover from the start of the river at the confluence of Silver Bow Creek and Warm Springs Creek down to the town of Deer Lodge. The width of the tailings deposits, as shown on the maps (the Vegetation Maps 7,8,9, and 10 from Appendix D, RIFR), was measured at 6-cm map intervals. The tailings may extend into vegetated areas; however, no vegetated areas were included in this preliminary determination of the tailings deposits area.

For the four maps, the average measured visible width of the tailings deposits is 38.8 meters on each side of the river, or 77.7

square meters of deposits per meter of river course. This area will be used for both calculations of the area of intersection of the saturated zone and the oxidation (and unsaturated) zone, and for the area from which erosion and runoff are predicted to occur by PRZM.

C and D represent, respectively, the adjustments to the measured surface area covered by the streamside tailings above the Warm Springs Ponds (along Silver Bow Creek) and adjustments to measured area below the Warm Springs Ponds (along the Upper Clark Fork River). Both C and D have a value of 1.0 if the measured surface area is used by the program NPSOUT in the contaminant loading calculations. Current calibrations of these two factors settle on a value of 1.0 for C and a value of 4.0 for D. These values indicate that initial measurements of tailings surface area may have not accounted for all the contamination along the Upper Clark Fork River below the Warm Springs Ponds.

SECTION 9

REMOVAL OF METALS IN THE WARM SPRING PONDS IN NPSOUT

To complete the model of metals transport from Silver Bow Creek to the Clark Fork River, a predictive description must be provided for the metal removal efficiency of the settling ponds (Warm Springs Ponds 3 and 2). The model will simulate reduction in metal fluxes at the segment juncture between the Silver Bow Creek and the Clark Fork River.

The NPSOUT program models the removal of copper in the stream at the end of Segment 6 of the surface water model (at the outlet to Warm Springs Pond 3). The approach taken with NPSOUT to account for removal of copper metal from the stream in the Warm Springs Ponds was to remove 80.4% of all copper loadings from sources to surface water segments 1,2,3,4,5, and 6.

The data shown in Table 22 are from the State of Montana (Ingman, 1986). The measured removal efficiency (mass removed/initial contaminant mass) of total copper (suspended and dissolved) between the station just above Warm Springs Pond 3 (Montana Water Quality Bureau Station 03) and the outlet of Warm Springs Pond 2 (Montana Water Quality Bureau Station 04) is 80.4% on average.

TABLE 22. Removal of Copper in Suspension and in Solution by Precipitation and Flocculation in the Warm Springs Ponds

Date of measurement	pH	Rate of Flow (ft ³ /sec)	Fraction Cu removed (% of mass flux)
10/28/1985	8.3	43.7	87.4
12/11/1985	7.9	30.5	81.5
1/6/1986	7.9	33.0	74.6
2/4/1986	8.0	41.3	79.1
2/25/1986	7.8	200.0	94.0
3/10/1986	7.8	69.9	64.8
4/7/1986	8.3	78.5	83.3
4/21/1986	8.9	73.7	88.9
5/5/1986	8.4	93.9	94.5
5/19/1986	9.0	93.9	79.1
6/2/1986	7.8	153.3	54.3
6/16/1986	8.5	64.3	83.8
Average Total Cu Removal:			80.4%
Median Total Cu Removal:			82.4%

The mechanism proposed for metal removal has been the combination of precipitation (with adsorption) and flocculation. Precipitation or adsorption of Cu and Zn should definitely occur as pH rises, as has been shown in the MINTEQA2 results, but the flocculation mechanism is not well-defined. Arsenic removal has a negative coefficient of correlation with pH, and this is possibly due to inhibition by OH^- of arsenate anion (AsO_3^-) adsorption or precipitation.

We can consider two cases. In the first case, little flocculation is occurring and this is not a dominant removal mechanism. Then metals are removed by precipitation and the settling of unflocculated precipitates. If settling is occurring at a regular velocity (for a smaller particle size, V_s or settling velocity is smaller), then more settling and a higher removal efficiency should occur for longer residence times in the ponds.

For the second case, flocculation is occurring, and is caused by a mechanism such as the counteracting (neutralization) of FeOOH acidic surface charges with $\text{Ca}(\text{OH})_2$ (lime), resulting in electrostatic repulsive forces being reduced and particle-particle combination occurring after interparticle collision and as a result of Van der Waal attractions between particles. Final removal rates would increase with increasing settling velocities and residence time in this case as well.

Regression analysis was performed on the above data set with both flow and pH independent variables (Figures 10 and 11). The results indicate little or no dependence of removal efficiency on flow. For instance, the coefficient of regression is positive for copper and negative for zinc and arsenic (indicating less zinc and arsenic removed with lower flow rates). In addition, the increase in R^2 with the inclusion of flow as a dependent variable is, respectively, 0.004, 0.004, and 0.21 for Cu, Zn, and As (out of a possible 0.879, 0.772, 0.992). These are small increases in explained variability.

R^2 is the ratio of SSR to SST. R^2 is also the ratio the sum of squares (explained variability) explained by the use of the variable to the total sum of squares (total variability).

The R^2 terms for regression of efficiency versus pH for Cu, Zn, As are respectively, 0.121, 0.228, 0.008. This leads to the deduction that some of the variability in pond efficiency can be explained with pH. However, the maximum R^2 value is 1.0, so much of the variability is left unexplained.

The seasonal determinants of pond efficiencies and the dependence of pond metal removal efficiency on flow and pH are not understood well enough to incorporate efficiency predictions into the metals loading model. There is a correlation of pond efficiency

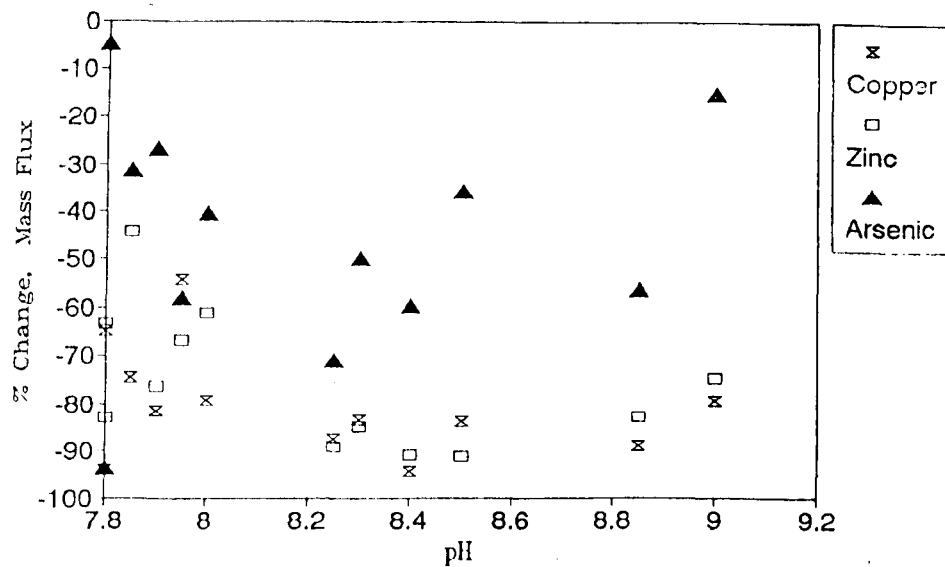


Figure 10. pH versus pond metal removal efficiency for flow through pond #3 and pond #2.

with pH (efficiency increases with pH for Cu and Zn and decreases with pH for As) (Figure 10). We can conclude that pond metal removal efficiency does depend on pH, so if pH can be predicted then values for pond metal removal efficiency may be improved.

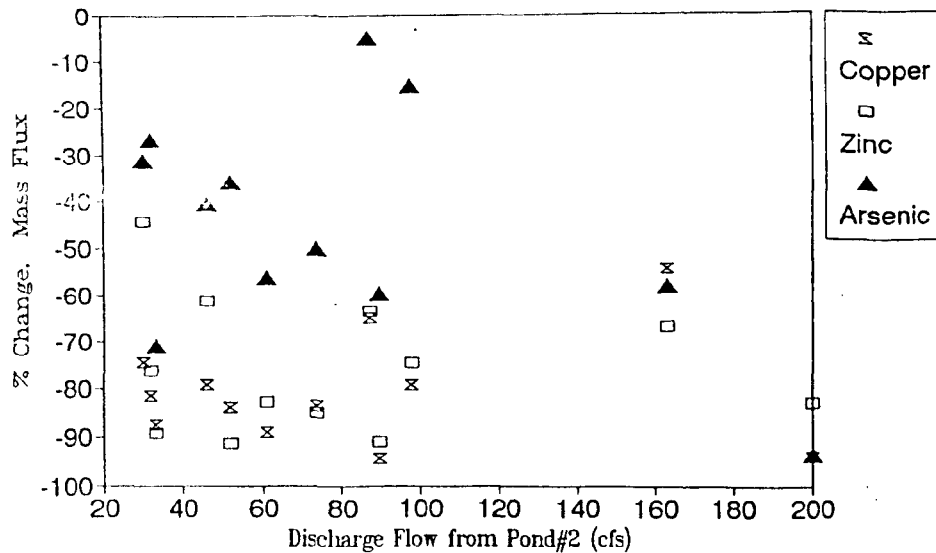


Figure 11. Flow through versus metal removal for flow through pond #3 and pond #2.

Since these data do not include a known flood peak, it may be that there are unidentified reductions in metals removal efficiencies at very high flow rates. Montana Water Quality Bureau Data from late 1986 and 1987 and RIFR data may show that strong correlations do exist and that the above results are anomalous.

Freezing-over of the ponds may lead to drastically reduced pond metal removal efficiencies due to short-circuiting of flows, although evidence that this occurs is as yet only anecdotal (Gary Ingman, personal communication).

The variables not included in the analysis above are seasonality, climatic history, and flow history. We believe that, in combination with these variables, it is likely that there is dependence of removal rate efficiency on flow rate and that residence time for the metal in the liming/precipitation ponds affects removal efficiency. The reason that there should be a correlation of flow to metal removal efficiency is that time of residence should be lower for a higher flow rate and flocculation of metal should occur at a lower rate, if the pond volumes do not vary significantly with flow rates or season.

SECTION 10

HYDROLOGIC AND HYDRAULIC STUDIES

This section summarizes the available hydrologic and hydraulic information on the site and describes the hydraulic modeling effort on the Silver Bow Creek-Upper Clark Fork River.

HYDROLOGY OF THE AREA

The area covering the Silver Bow Creek watershed has a continental climate, that is characterized by short, cool, dry summers and long cold winters. Annual precipitation may vary from 6 to 20 inches with an average of approximately 12 inches. Climate in the upper Clark Fork Valley is about the same and the average precipitation is 13.2 inches. In general 50% of precipitation falls in the late spring and early summer, which if augmented with snowmelt can cause severe flooding. The majority of the annual stream flow comes from melting of the snow packs. Streams can easily become partially or fully ice covered during winter season. Although maximum flow in Silver Bow Creek and Upper Clark Fork River occurs in late spring and early summer, on smaller sub-watersheds maximum flow may occur in winter by rainfall on frozen ground. Cloud bursts and thunder storms may occur in late the summer season.

Hydrologic investigation of the area (CH2M-Hill, 1988) has shown that the Probable Maximum Flood (PMF) peak at the diversion into Warm Springs Pond 3 is about 117,200 ft³/sec with a total volume of 191,000 acre-feet. Also flow entering ponds in excess of 5600 ft³/sec would cause the overtopping of Warm Springs Pond 3, floods in excess of 7000 ft³/sec would overtop Warm Springs Pond 2, and flows in excess of 7500 ft³/sec would overtop all three ponds. As a result of overtopping, the pond embankments would fail due to erosion and subsequent gullyng. In addition, sediment volumes delivered to the ponds is estimated to be 25,000, 50,000, and 100,000 cubic yards for 10-, 25-, and 100-year floods, respectively. Therefore, as time goes on, the capacity of the ponds to hold water decreases and the probability of failure due to floods increases. The above reference provides a table of historic floods in the area as well as details of sub-watersheds hydrology and peak flows for tributaries.

HYDRAULICS AND FLOW MODELING

The main path of Silver Bow Creek and the Upper Clark Fork River can best be described as meandering with top width varying from 10 to 50 ft. The cross sections are close to rectangular in the main channel with deeper points near one of the banks. The flood plains, which could be very wide at some locations, often are

covered with small bushes, trees or grasses. The bottom materials are mostly sand, cobbles, and boulders that result in high roughness coefficients. The stream has a high bottom slope (on the average 0.42%) and, consequently, its velocity is high even during normal flows. Many perennial and ephemeral tributaries feed the stream along its course from Butte to Deer Lodge making it a gaining stream. In the top reaches of Silver Bow Creek above the confluence with Blacktail Creek, the stream may go dry during mid to late summer but the flow may still exist under the immediate stream bottom layer in the form of underflow through the alluvial aquifer that underlies the valley floor. Because of the high slope and the consequent transport of finer particles even during the low flow periods, the bottom materials are coarse except on the flood plains and in the overbank regions where finer materials may be found. Flow is seldom uniform or laminar and, for all practical purposes, it can be assumed as turbulent everywhere and at all times. Many structures such as bridges, diversions, etc., which can alter the flow regime are built in the stream path. The major structures are the Warm Spring Ponds and their control facilities. These structures are primarily built to treat the Silver Bow Creek waters before entering the Upper Clark Fork River, although they could serve as a flow regulator during flood periods. Flows in excess of the ponds' control structure capacities are not treated and are bypassed through Mill Willow Creek extensions.

As this brief introduction shows, the hydraulics of the Silver Bow Creek-Clark Fork River combination is complex and the hydrodynamic modeling effort requires a good feel for the area and some innovation to adapt standard river models to the problem. This difficulty is compounded further by the lack of adequate information. In the following discussion the details of hydraulic modeling are explained.

HYDRAULIC MODELING

The model applied in this project is an extended and modified version of the unsteady river hydrodynamic model developed by Amein and Fang (1970) and later updated and used by Fread and Smith (1978) as well as others. In our application, the model is modified to transport sediment in the sand size range and to accommodate time-variant lateral inflows as well as interfacing with the WASP4 water quality modeling package.

The model uses the Saint Venant equations for fluid flow, and sediment yield and sediment continuity equations for particulate transport. The sediment yield equation used in the model is the Yang's total load formula. Two forms of the sediment continuity equations are used to account for scour/deposition and bed level variations. The Four Point Implicit numerical scheme which is fully stable, efficient and accurate is adopted for the time integration. Nonlinearity is treated by the Newton-Raphson iterative technique.

The flow equations are solved simultaneously for depth and discharge at all cross sections. From these parameters flow velocity, channel width and hydraulic radius are calculated to be used for the computation of bed shear velocity and velocity for incipient motion. These variables and the particle fall velocity then are used in the Yang's equation to find the sediment flux at a given cross-section. The sediment flux is used in the sediment continuity equation in combination with lateral sediment inflow, to calculate the sediment cross-sectional change from which the determination of scour and deposition is made. Although the sediment module was not activated in this application, it has been used in other projects (Hosseini pour, 1989).

MODEL EQUATIONS

The river flow and sediment transport model described herein uses two sets of equations. The first set is the Saint Venant equations for flow and the second set consists of the sediment yield and sediment transport continuity equations for the longitudinal transport and bed level changes.

FLOW EQUATIONS

The one-dimensional equations of unsteady state flow used in the model consist of the equations for the conservation of mass and momentum. Derivation of the various forms of the equations are given by Chow (1959) and Henderson (1966). Expansion of the equations into the Finite Difference forms and implicit time integration scheme is described in detail by Amein and Chu (1975) and Hosseini pour (1989).

SEDIMENT TRANSPORT AND SEDIMENT YIELD EQUATIONS

The sediment yield equation used in the modification of the hydrodynamic model is the sand transport equation proposed by Yang (1973). The transport of the sediments in the stream is simulated by incorporating the sediment continuity equation into the flow model. The flow equations and the sediment transport equation are then solved for the model network uncoupled.

Theoretical development of these equations are given by Garde and Ranga Raju (1985), Yalin (1977) and others. Application of the equations are reported by Chang (1982) and by Chang and Hill (1976). These equations account for sediment cross sectional variation with time and sediment yield variations with distance along the stream. Figure 12 below depicts a typical erodible channel cross section and the associated sediment profile.

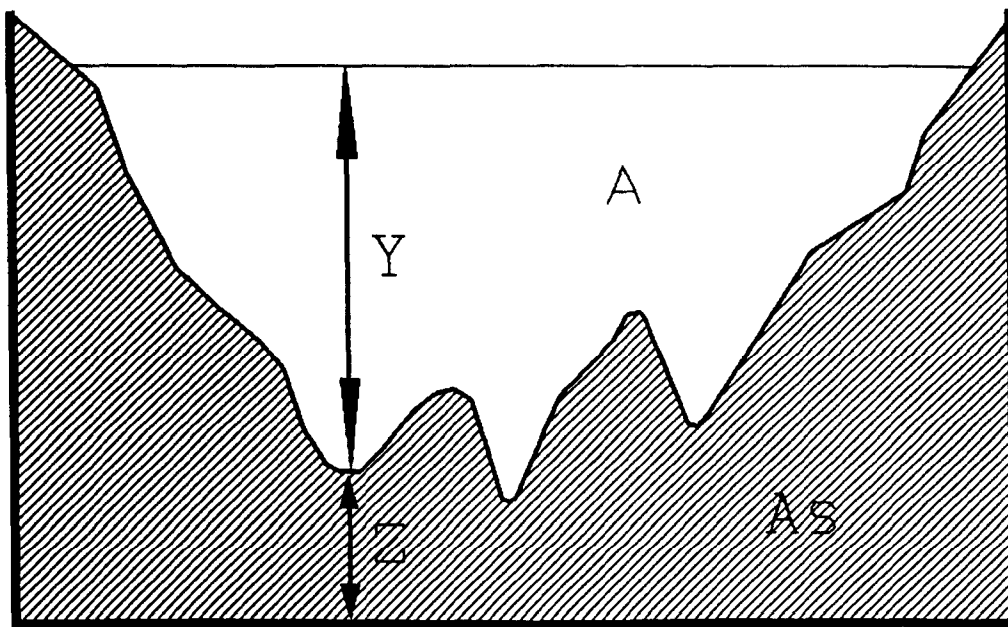


Figure 12. Cross-section of a typical erodible channel.

DATA REQUIREMENTS

The model described above requires two kinds of data: hydraulics and sediments information. The hydraulic data include channel morphometry, bed elevations, and initial and boundary conditions. The sediment data include sediment median size, sediment porosity, specific weight, water viscosity and channel roughness. If cross-sectional topography data are available then a separate sub-model can be used to generate exponential rating functions for cross sections and wetted perimeters as a function of depth in the form of $A=c+a_2 \cdot y^{b_2}$ and $P=d+a_1 \cdot y^{b_1}$ for natural streams. The sub-model uses the topographical coordinates to generate these relationships for every cross section. The variables are defined as: A is the cross sectional area, y is the depth at the given cross section, and the rest are constants calculated by the sub-model. The model then uses these relationships to calculate automatically the area and wetted perimeter as the water depth changes. This feature allows the model to use natural cross sections and therefore simulations are closer to the natural behavior of the stream.

SILVER BOW CREEK-CLARK FORK RIVER APPLICATION OF THE MODEL

The model was applied on the 52.6 mile stretch of the Silver Bow Creek-Clark Fork River from Butte down to Deer Lodge. Since the hydraulic characteristics of the Warm Spring Ponds is very different than the stream channel, the flow modeling was done through the by-pass around the ponds. Various segmentations and cross sections were used in the initial trial runs to check the adaptability of the model to the problem. The final runs were made using the natural cross sectional topography from the maps of the hydrologic investigations. According to these maps, which were also verified on a site visit later, the main channels are from 10 to 50 feet wide and are roughly rectangular in shape. The model was run with 30 segments initially and later the number of segmentations were reduced to 11 to increase the efficiency as well as to match the stations where water quality parameters were available. No significant discrepancy in the hydraulic modeling results were observed as a result of reduction in the number of segmentations. The report on the hydrological investigations provided the Manning's roughness coefficient in the range of 0.045 to 0.055 for the main channel and 0.075 to 0.15 for over bank flooding areas. These figures were used to calculate the composite roughness coefficient for the high flow scenarios in the modeling effort. The formula used to calculate the composite roughness was chosen from the Chow's book which has the form

$$n = \left[\frac{\sum_{i=1}^N P_i n_i^2}{P} \right]^{1/2}$$

where p_i is the portion of the perimeter with roughness value of n_i , P is the total perimeter and n is the composite roughness.

The USGS data files on the streams provided three useful discharge measurements on the Silver Bow Creek, Warm Spring Creek, and Clark Fork River at Deer Lodge that could be used in modeling studies. Five scenarios were chosen in flow modeling which represented the different flow situations throughout the year in the streams. These included normal winter and late summer low flows, late spring and early summer high flows, and flash floods due to cloud bursts and thunderstorms or sudden snow melts. The boundary conditions were assigned as upstream discharge at Butte, estimated time variant lateral inflows, and downstream stage at Deer Lodge. Since only discharge measurements were provided at Deer Lodge, the Manning equation was used to estimate the stage corresponding to the given discharge. Further, since great variations in the discharges at the three gauging stations were present, the time variant-tributary inflows were adjusted to match the total flow at Deer Lodge. The incomplete data available on some other stations along the stream provided an insight in the adjustments of tributaries flows.

SECTION 11

RESULTS

SURFACE WATER MODELING RESULTS

The in-stream copper concentration predictions for the Upper Clark Fork River basin have been compared to measured surface water concentrations. The comparison has been examined, as has the modeling system and the assumptions used, for observations about the usefulness of our approach.

Each subsite has a final calibrated value for K_d and for Q/V . Other parameters and their values at subsites are shown in Table 23. These include values for time of travel to open water from the sub-tailings aquifer and the lifetime of the contaminant pulse.

Q/V is the parameter that represents the ratio of the horizontal velocity in the aquifer to the effective tailings deposit width on one side of a perennial stream (for the case of a streamside deposit) or an intermittent stream (for the case of off-stream waste subsites).

TABLE 23. Superfund Subsite NPSOUT Final Parameters

Superfund subsite	K_d	Lifetime of contaminant pulse (days)	Q/V (day ⁻¹)	Time of travel to open water (days)
Butte	1300	120	0.24	0
Silver Bow Creek (stream side)	234	120	0.12	0
Anaconda smelter	503	12	0.04	0
Clark Fork River (stream side)	234	3	1.0	0

RESULTS OF TRIBUTARY AND MAIN DUMP SITES

The surface water modeling results of this study are summarized in the following manner. First, the copper concentrations in Silver Bow Creek, the Mill-Willow Bypass, and Warm Springs Creek are compared with the predicted metal loadings from the off-stream subsites. The subsites include the Butte mine drainages and all other subsites for segment 1 (including the Yankee Doodle Tailings, the waste rock dumps, and the Butte Active Mine Area, with active mining and milling sites) and the Anaconda Smelter with the other subsites for segment 7 (including the slag piles and the Opportunity Ponds).

The contaminants at the end of segment 1 are taken as a measure of the Butte source terms, such as the principal Butte waste dump seepages and drainages. The principal drainages and seepages from the Anaconda smelter area (Mill-Willow Bypass streamside tailings, Opportunity Ponds seepages, Mill-Willow Creek basin, Warm Springs Creek basin) enter segment 7. The measurements of loadings into segments 1 and 7 are used as reference data for the calibration of the NPSOUT model for contaminant sources in Butte and Anaconda. During high flows, these off-stream source terms may not describe the entire metal flux observed in the stream but they should represent 50% to 100% of the copper loadings during medium and low flows.

Predictions of copper flux from the tributary sites (Mill-Willow Bypass, Warm Springs Ponds) were performed with NPSOUT, and the results are compared with a selection of 15 measurements that date from 1984 through 1986 (Ingman, 1987). This comparison is made graphically by plotting loading estimates from model runs versus tributary loading data (Brown, 1989).

The first two sets of comparisons (Figures 13 through 16) show how increasing K_d reduces the predicted metal fluxes and improves the resemblance between model predictions and the measured data for segment 1 and segment 7.

Figures 16 and 17 demonstrate the results of a change in the Q/V ratio parameter (variable TQDIVV in the model) for the off-stream subsite sites and an improved resemblance to the calibration data for Segment 7. This change is equivalent to a large increase in the rate of flow from the aquifer. Contaminant pulse lifetime is kept at 120 days for all calibrations of the off-stream subsites. Travel time of the contaminant pulse front to surface water has been kept at 0 days.

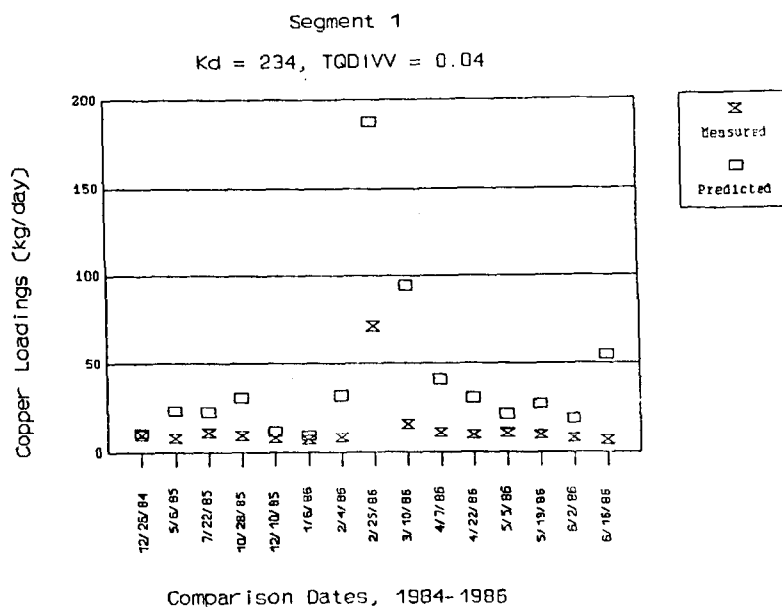


Figure 13. Measured versus predicted copper loadings, segment 1.

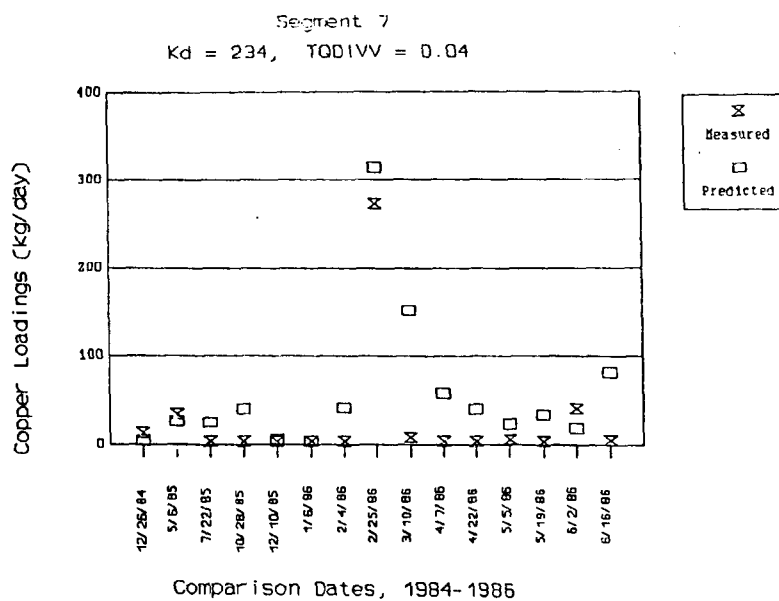


Figure 14. Measured versus predicted copper loadings, segment 7.

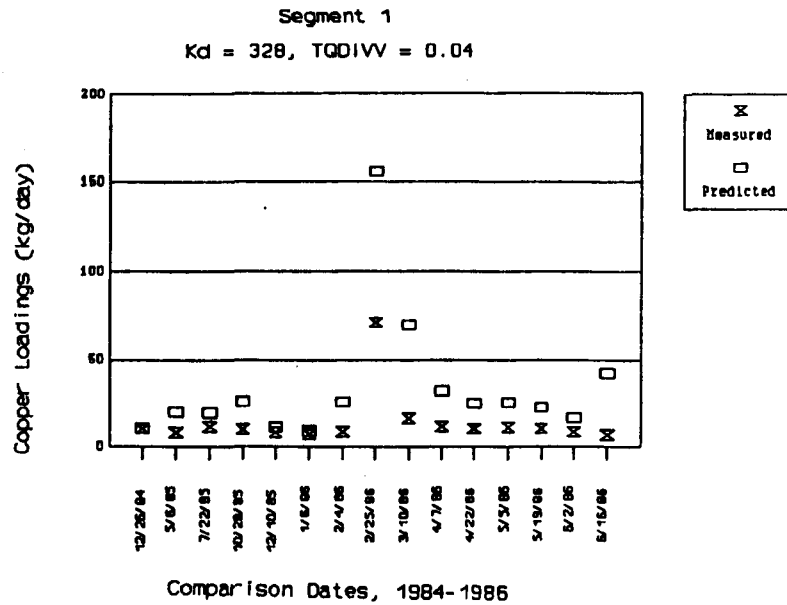


Figure 15. Measured versus predicted copper loadings, segment 1.

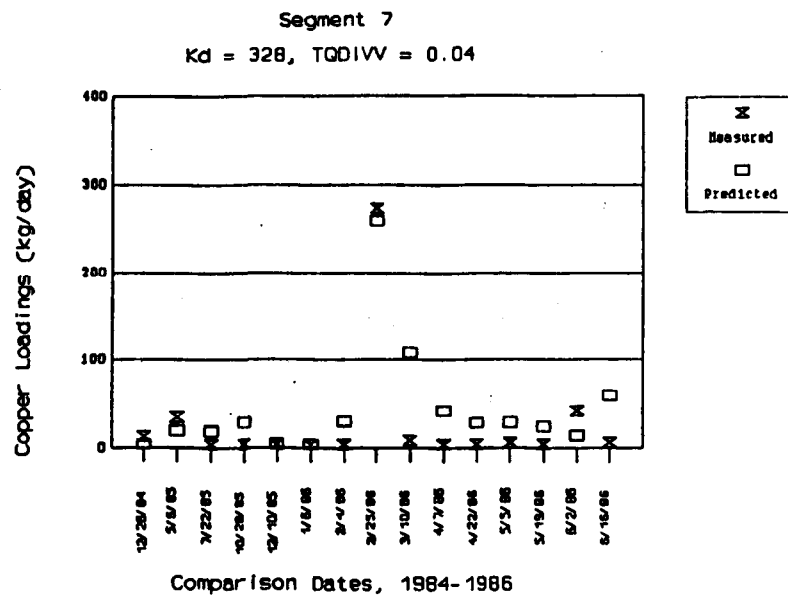


Figure 16. Measured versus predicted copper loadings, segment 7.

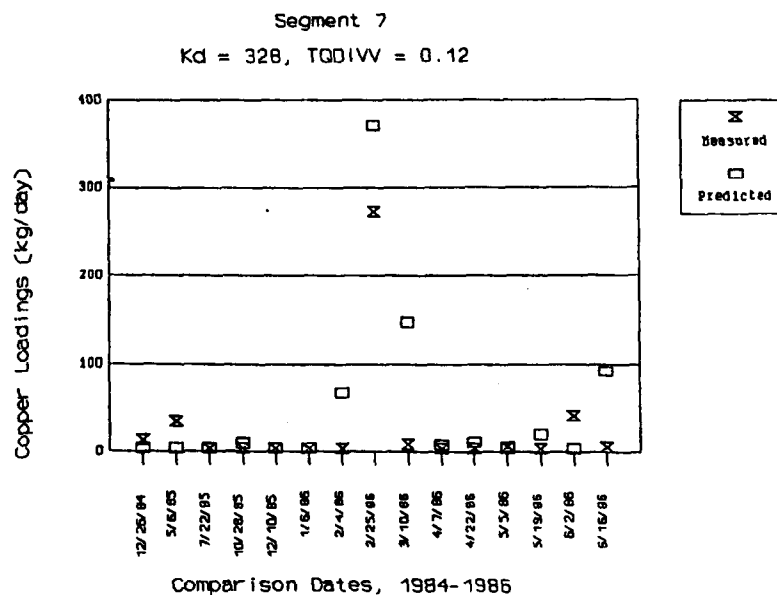


Figure 17. Measured versus predicted copper loadings, segment 7.

The type of groundwater transport and mixing model used substantially controls the prediction of copper loadings into the surface water. Other possible changes to the groundwater mixing model would be to include more than one mixing volume. The efficiency of mixing in the aquifer also might be changed in order to improve the model. The Q/V parameter changes the rate of flow represented but not the efficiency of mixing or the number of mixing volumes in the aquifer.

The PRZM model results also demonstrate the predictions for copper loadings depend on the partition coefficient K_d . A more realistic model might vary the partition coefficient within a given subsite, but the current approach does not provide for that possibility. The use of a single soil core geochemistry (2-dimensional isotropy) for each subsite is the most significant assumption in the model. Figures 13, 15, and 18 compare concentration predictions for several values of K_d with measured surface water copper concentrations.

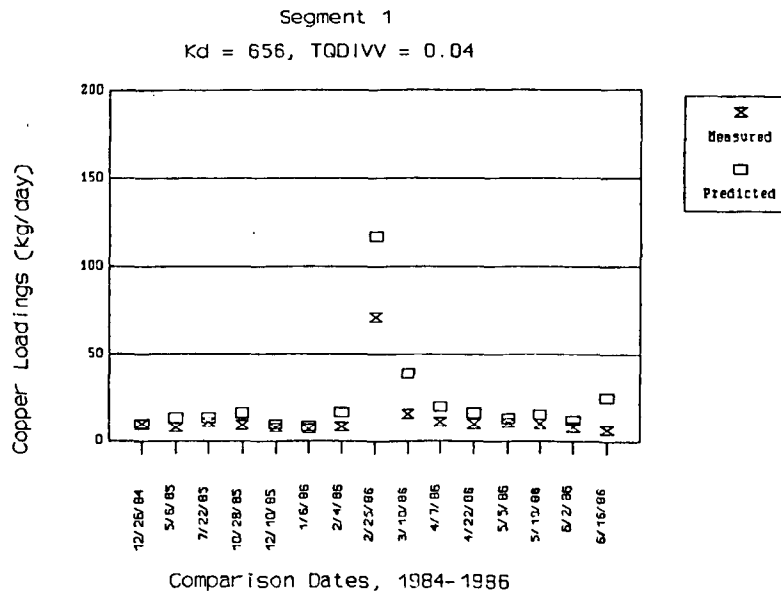


Figure 18. Measured versus predicted copper loadings, segment 1.

IN-STREAM PREDICTIONS

The final calibrated parameters for the model are shown in Table 23. The in-stream modeling effort is based upon generating stream hydraulics and loadings for five different meteorological and flow scenarios. Two flood periods were examined - a typical winter flood due to runoff and a typical spring flood due to snowmelt. The seasonality of the flow periods and contaminant transport rates has already been discussed. Figures 19 through 22 below show the model predictions for the above scenarios.

Parameters chosen for the streamside tailings on Silver Bow Creek were as follows. Q/V (the NPSOUT variable QDIVV) was 0.4 1/days and the contaminant pulse lifetime was set at 12.0 days. For the streamside tailings along the Clark Fork River, Q/V was set to 1.0 1/days, the pulse lifetime was set to 3.0 days for all cases, and the travel time was set to 0.0 days.

In Figures 23 through 26, the comparisons between the concentrations of copper measured for normal winter and normal spring flow and model predictions are shown. The normal flows for spring and winter were also examined.

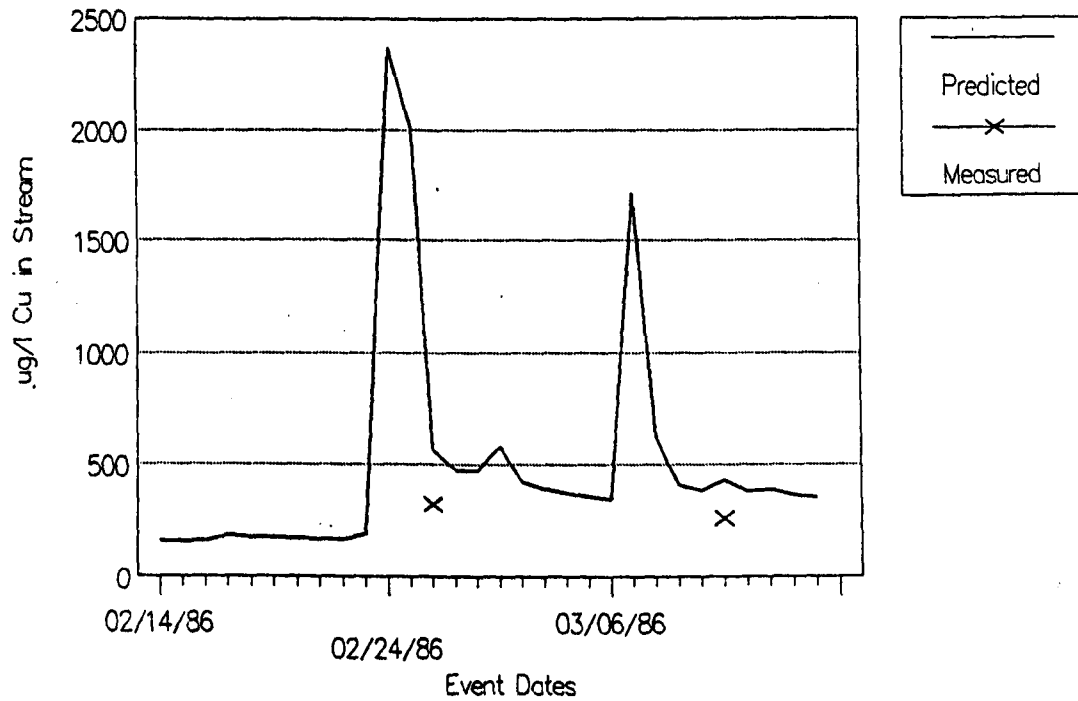


Figure 19. Predicted and measured winter floods, segment 1.

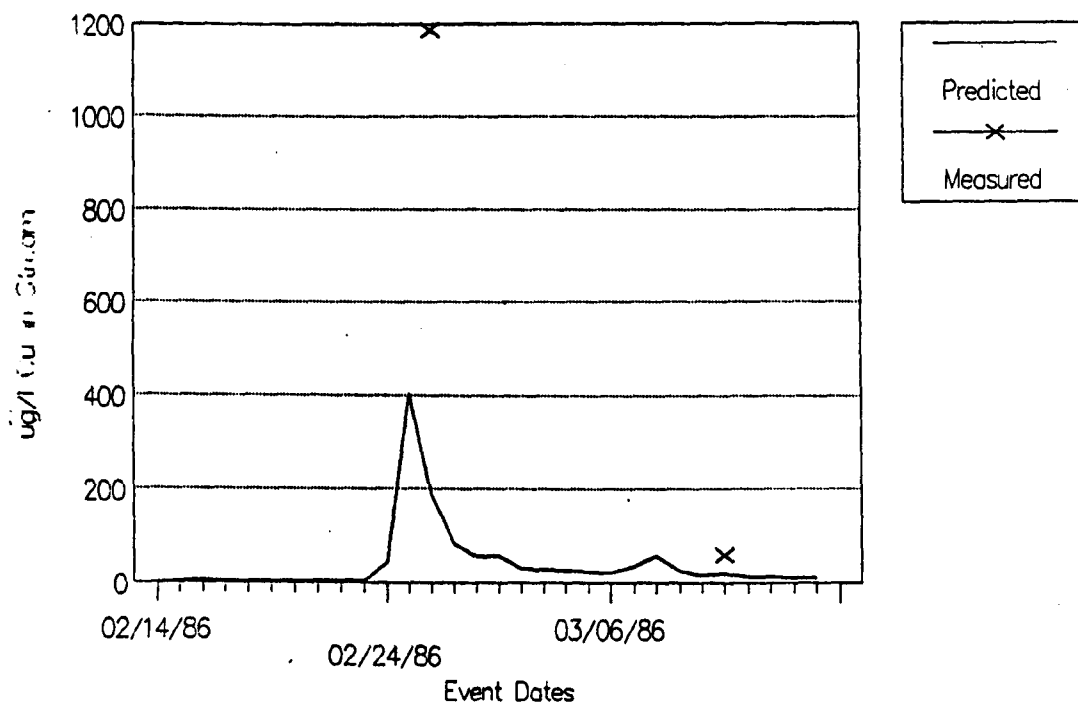


Figure 20. Predicted and measured winter floods, segment 11.

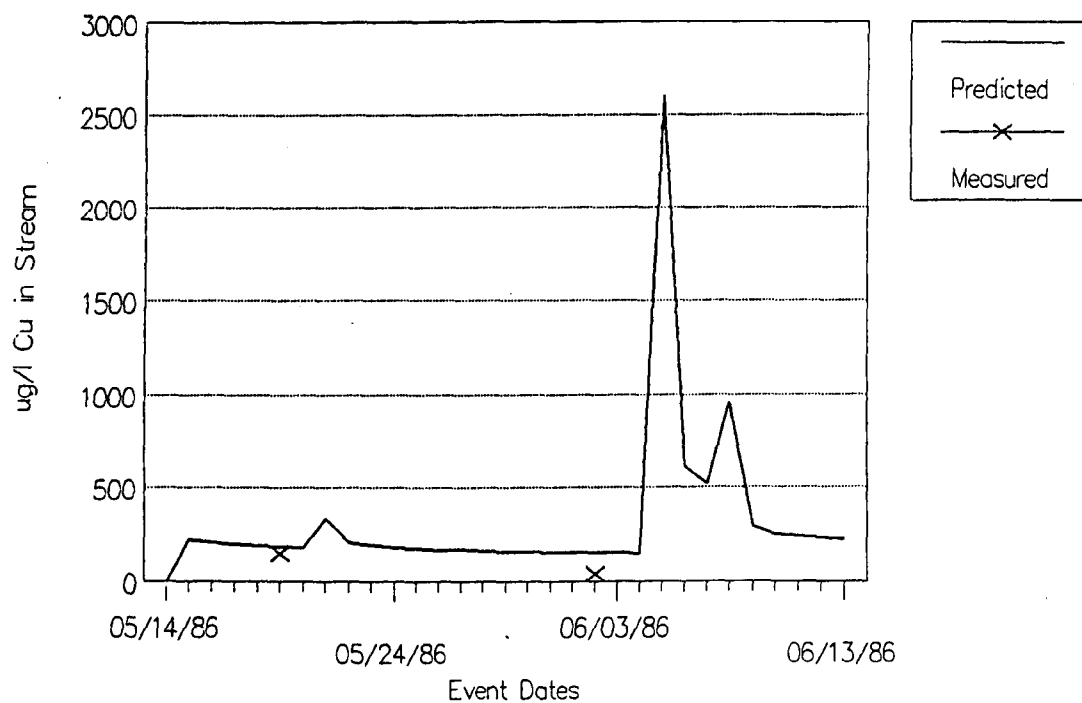


Figure 21. Predicted and measured spring floods, segment 1.

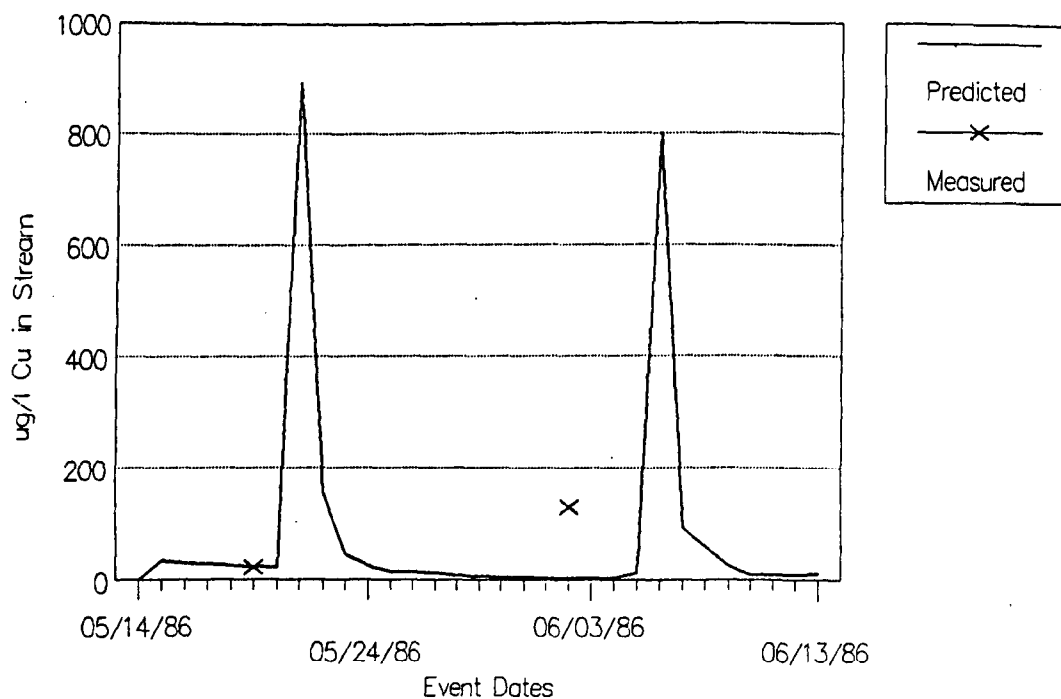


Figure 22. Predicted and measured spring floods, segment 1.

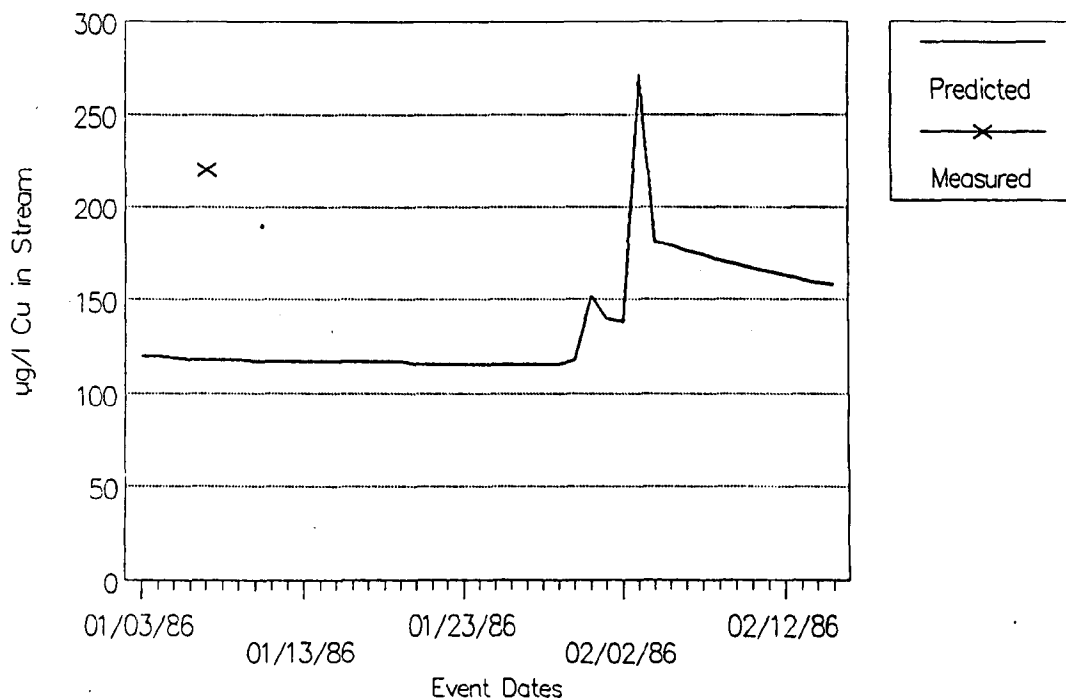


Figure 23. Predicted and measured normal winter flows, segment 1.

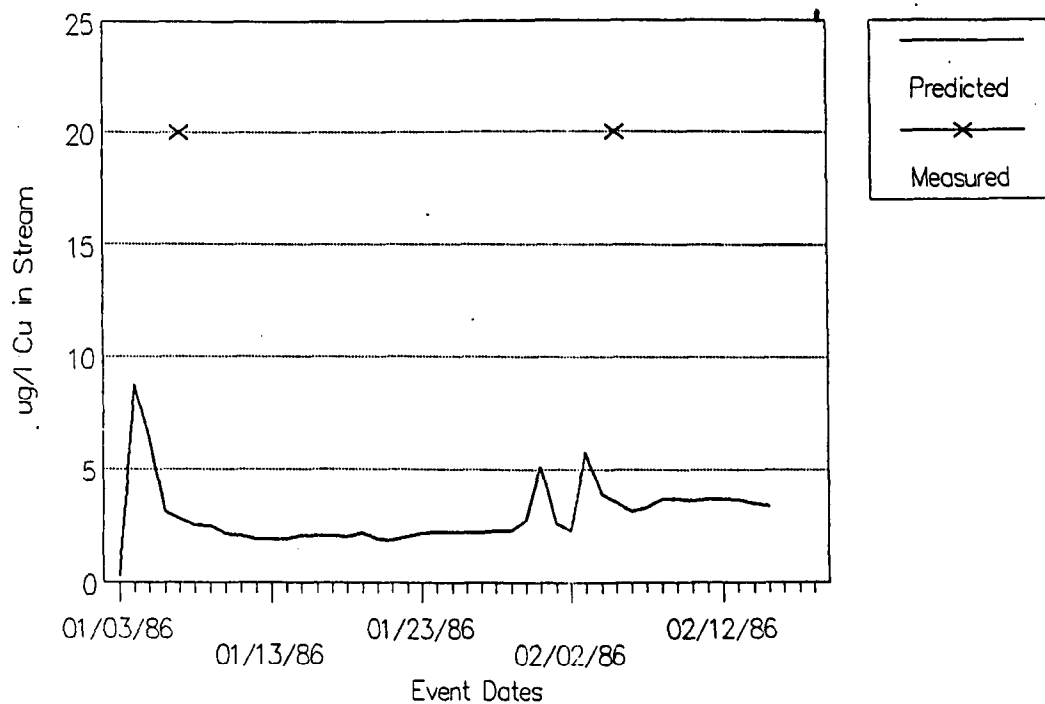


Figure 24. Predicted and measured normal winter flow, segment 11.

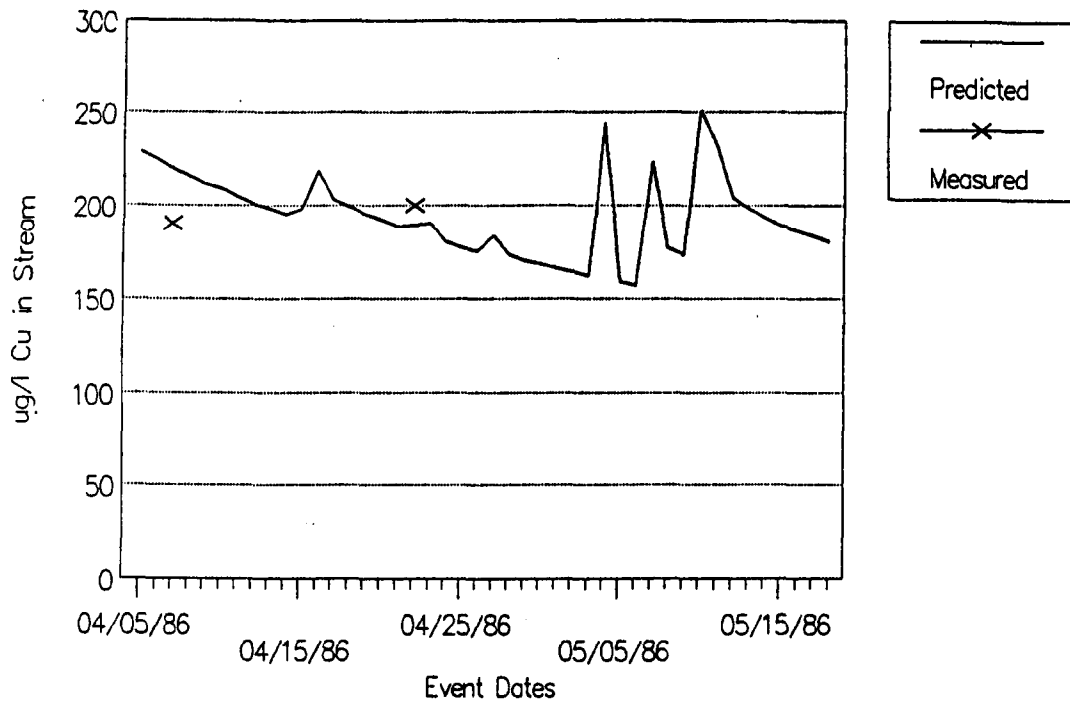


Figure 25. Predicted and measured normal spring flow, segment 1.

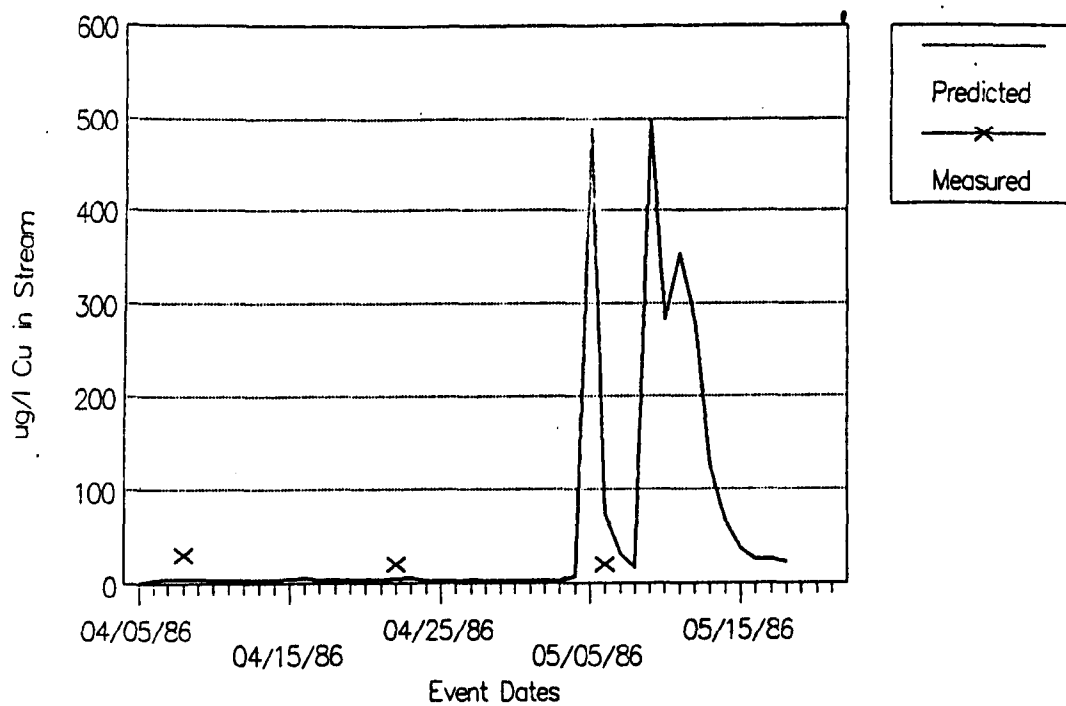


Figure 26. Predicted and measured normal spring flow, segment 11.

Finally, the low flow periods during late summer and the fall were examined (see Figures 27 and 28). Without having experimental data for comparison, one can nonetheless observe the severity of the predicted high copper concentration in the stream during low flow periods.

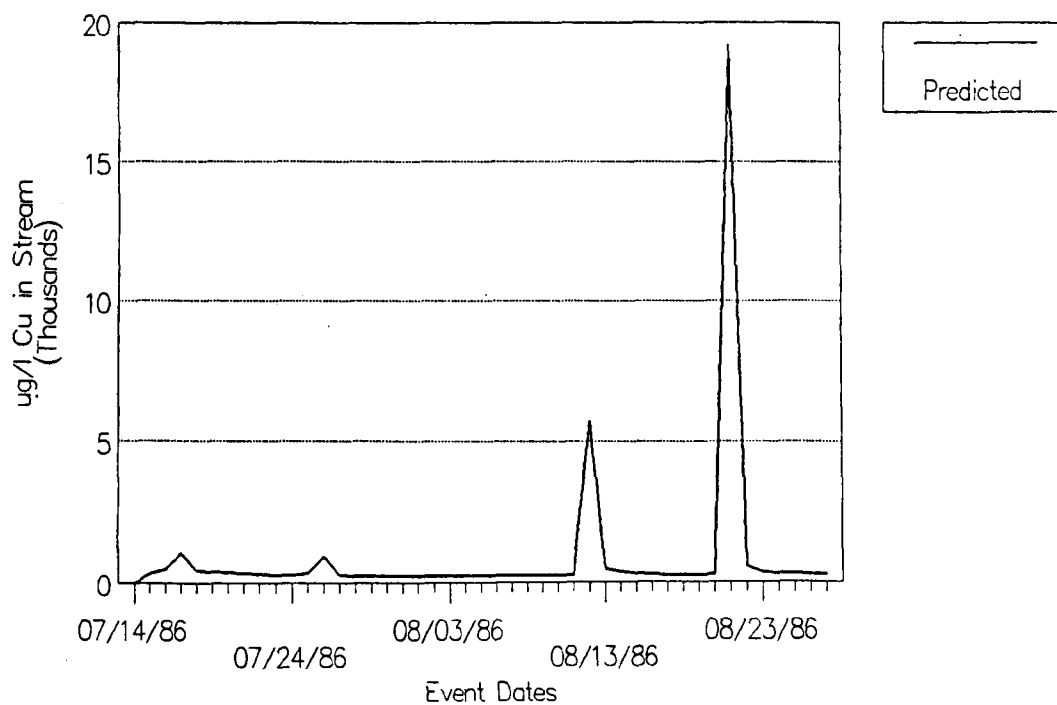


Figure 27. Predicted normal fall-summer flow, segment 1.

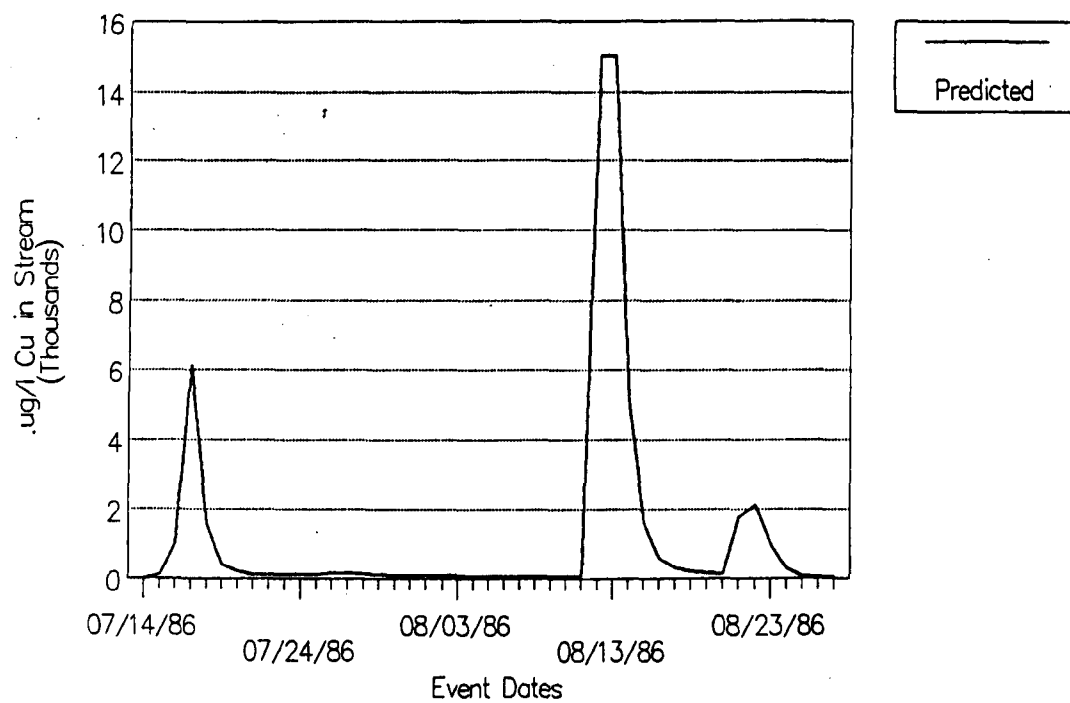


Figure 28. Predicted normal fall flow, segment 11.

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