ENVIRONMENTAL RESEARCH REPORT
HYDRAULIC AND WATER QUALITY MODELING OF SILVER BOW CREEK-UPPER CLARK RIVER, A SUPERFUND SITE IN 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 CEAM modeling 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 to the site to show the applicability of such modeling schemes and the complexities involved in this application. Some of the models had to be modified to match the physics of this project. Graphs of the water quality parameters show good fit between the measured and predicted concentrations at some stations while substantial deviations are observed at other stations along the course of the stream.

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 brief describes one such demonstration project - analysis of metals contamination of the upper Clark Fork River, Montana.

INTRODUCTION

This project was initiated to analyze the hydrology and water quality of the Silver Bow Creek-Clark Fork River 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. The Superfund site includes Silver Bow Creek with the Warm Springs Ponds, and the old mine and dump sites at Butte. Remedial Investigation

has been conducted in the Silver Bow Creek region and a set of reports that comprise the Silver Bow Creek Remedial Investigation Final Report (RIFR) have been prepared (Tuesday et. al., 1987).
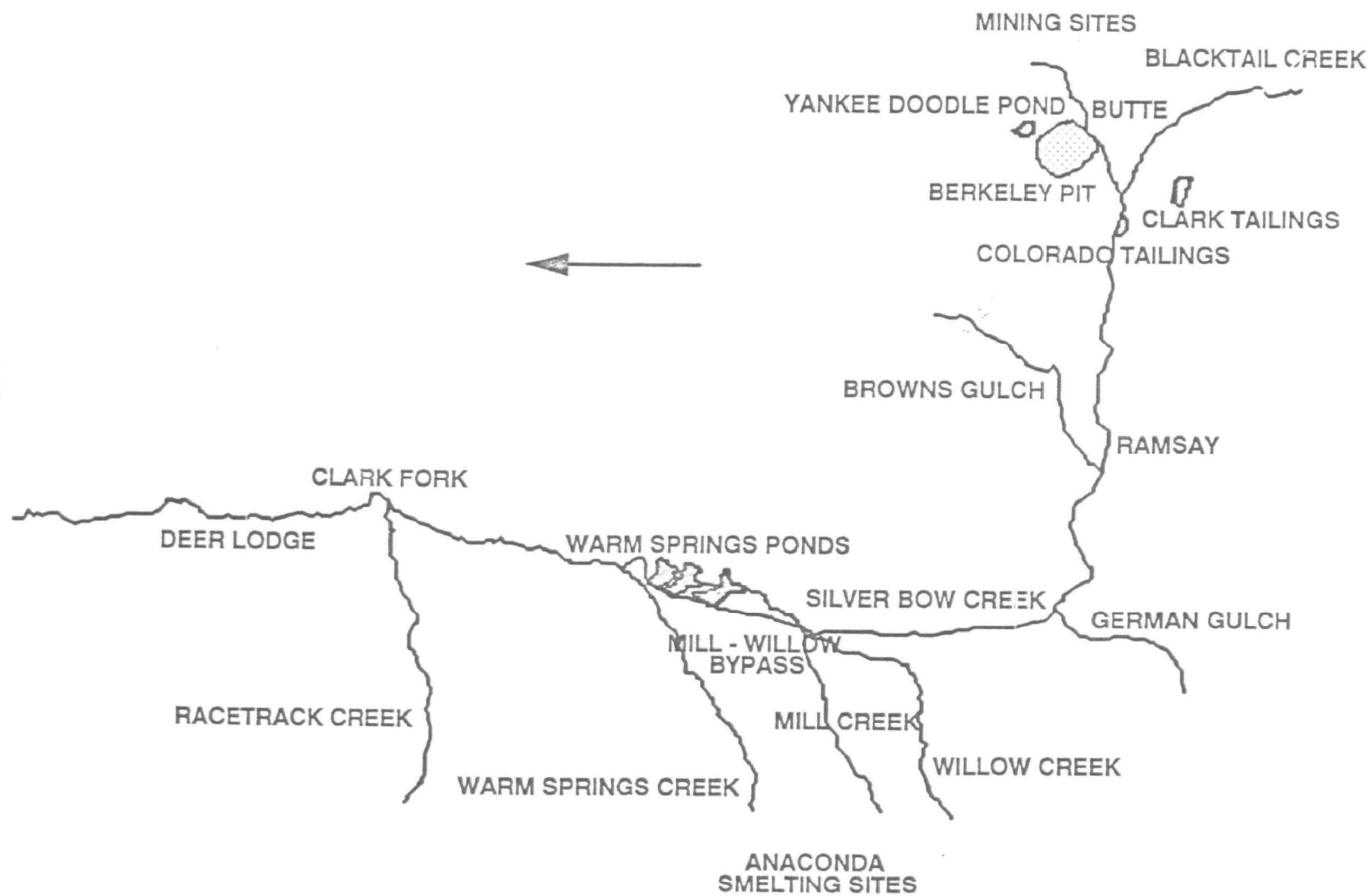
Description of the Study Area

Silver Bow Creek flows as a small stream from Butte at the Metro Storm Drain, to the Warm Springs Ponds 27 miles downstream. Both acid 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. The stream flows through Pond 3 (100 hectares of open water) into Pond 2 (32 hectares) and into Pond 1 (8 hectares). Sediment deposits rise above the surface of these shallow ponds. Below Pond 2 the creek reaches the confluence with the Mill-Willow Bypass, which drains the waste sites surrounding the Anaconda smelter, the flows from Mill and Willow Creek, and seepage from the Warm Spring Ponds. Below this confluence, the creek combines with the flow from Warm Springs Creek and becomes the Upper Clark Fork River. The creeks that enter the river below the Warm Springs Ponds include Modesty Creek, Lost Creek, Dempsey Creek and Racetrack Creek, and a substantial increase in flow occurs. (Figure 1)

More than 100 years of continuous mining operations and related activities have changed the area's natural environment greatly. Waste rocks, ore process tailings, acid 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. Settling ponds have limited capacity and during high flows (discharges of greater than 700 cfs) the flow is by-passed without any treatment. Further, geotechnical studies have revealed that a flow of 4000 cfs 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 cfs (Ch2M-Hill 1988). The Remedial Investigation Final Report indicates that the seepage from under the Warm Springs Ponds can act as a major source of ground water pollution. Toxic elements from tailing deposits are 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 as a high priority Superfund site. As this brief introduction indicates, 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

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Upper Clark Fork Basin of
Silver Bow Creek Superfund Site

MINING SITES

BLACKTAIL CREEK

YANKEE DOODLE POND BUTTE

BERKELEY PIT

CLARK TAILINGS

COLORADO TAILINGS

BROWNS GULCH

RAMSAY

CLARK FORK

DEER LODGE

WARM SPRINGS PONDS

SILVER BOW CREEK

GERMAN GULCH

MILL - WILLOW BYPASS

RACETRACK CREEK

MILL CREEK

WILLOW CREEK

WARM SPRINGS CREEK

ANACONDA
SMELTING SITES

employed to delineate the pathways and the fate of pollutants.

History of Metals in the River

Since 1866, 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 rock that was removed as backfill and overburden from either pit mines or underground mines 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 stream bed.

Between 1918 and 1920, 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. These ponds were originally 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, treatment efficiency declined and particles remained suspended in the effluent. To remedy the problem a larger pond was constructed above the first two ponds between 1953 and 1959. Pond 3 was improved between 1959 and 1969 to increase the capacity for metal removal.

Lime was added to the ponds to precipitate and flocculate the metals. This method of settling the metal colloids and particles from Silver Bow Creek is 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 the flow is directed to 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 smelting 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. In some areas, the sediments have released sufficient metal to either limit plant growth to metal-tolerant species or eliminate plant

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coverage entirely. 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 of 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 metal contaminants, such as iron, aluminum, zinc, copper, arsenic, lead, and cadmium.

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 settling ponds and enter untreated into the Upper Clark Fork River. Such events are known to have caused mass fish kills in the Clark Fork River.

Objectives of the Study

The modeling effort at the Center for Exposure Assessment Modeling (CEAM) will focus on the prediction of the frequencies of exposure of fish to toxic metals at different concentration levels in the stream by using the 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 modelled by US EPA, ERL at Duluth.

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 transport of heavy metals into the stream were analyzed in the following manner. 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 predicted by MINTEQA2 (Brown et al. 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 (Hosseinipour, 1988). The toxicity evaluations will be performed by a Fish Acute

Toxicity model developed at the ERL-Duluth (Figure 2).

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. A substantial body of scientific literature already exists on the chemical processes that create acid mine drainage from mine wastes. What is known about the mine and process wastes is summarized below.

The sidestream tailings deposits are sandlike fine particles of metal sulfides. The primary 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 are geologically embedded in monzonite porphyry (primarily feldspar).

The ores are blasted, then mined, crushed, and leached during the initial processing steps. Smelting is an oxidative roasting process that leaves slag as process waste. Mechanical reduction in size of the ore particles increases the availability of surface area for oxidation of the sulfide minerals.

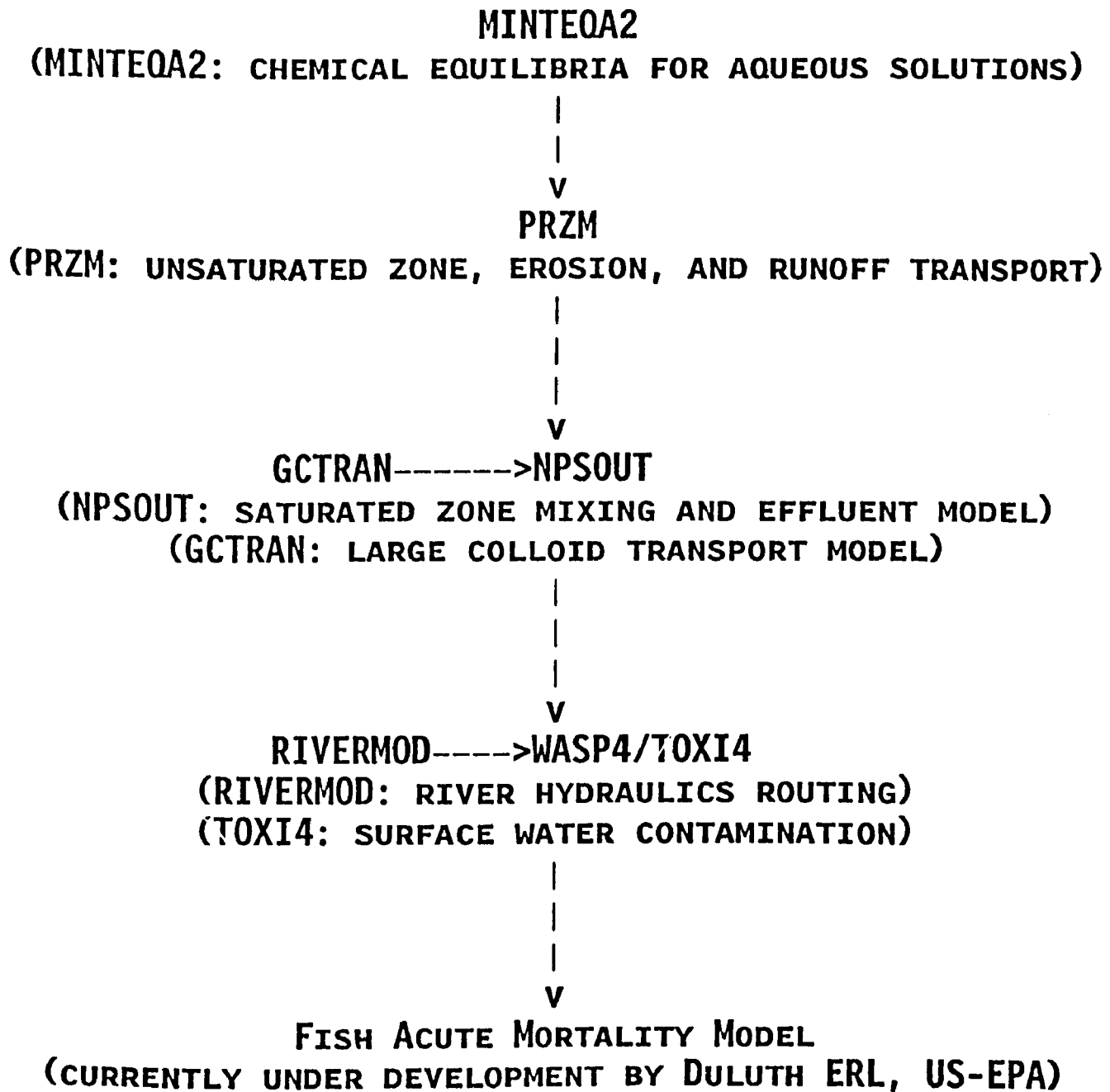The source of the copper is assumed to be a sulfide-bearing waste tailings particle that is corroded by exposure to water and oxygen. The limits on metal transport and solubility will determine the magnitude of the tailing's role as sources of contaminants to the river, and under certain circumstances MINTEQA2 can be used to indicate the partitioning of metal between soil and water. 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 depth. pH is set by advection and diffusion of H^+ away from the particle. pH is increased 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 sulfides react with oxygen and water to form metal ions and sulfuric acid. The process of oxidation is dependent on a supply of reactants (water, sulfides, oxygen) and on water as a transport medium for reactants and products. The process of oxidation must be limited by transport of product or reactants; otherwise rock sulfides would not exist in native form.

Oxygen is transported from the surface of the tailings where oxygen in the water phase is in equilibrium with the atmosphere. Oxygen diffuses into the tailing deposit on the

FIGURE 2

DIAGRAM OF THE MODELING SYSTEM USED

IN THE CLARK FORK RIVER EXPOSURE ASSESSMENT

MINTEQA2

(MINTEQA2: CHEMICAL EQUILIBRIA FOR AQUEOUS SOLUTIONS)

|
|
v

PRZM

(PRZM: UNSATURATED ZONE, EROSION, AND RUNOFF TRANSPORT)

|
|
|
v

GCTRAN------->NPSOUT

(NPSOUT: SATURATED ZONE MIXING AND EFFLUENT MODEL)

(GCTRAN: LARGE COLLOID TRANSPORT MODEL)

|
|
|
v

RIVERMOD---->WASP4/TOXI4

(RIVERMOD: RIVER HYDRAULICS ROUTING)

(TOXI4: SURFACE WATER CONTAMINATION)

|
|
|
v

FISH ACUTE MORTALITY MODEL

(CURRENTLY UNDER DEVELOPMENT BY DULUTH ERL, US-EPA)

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 unsaturated zone oxidized soil stratum.
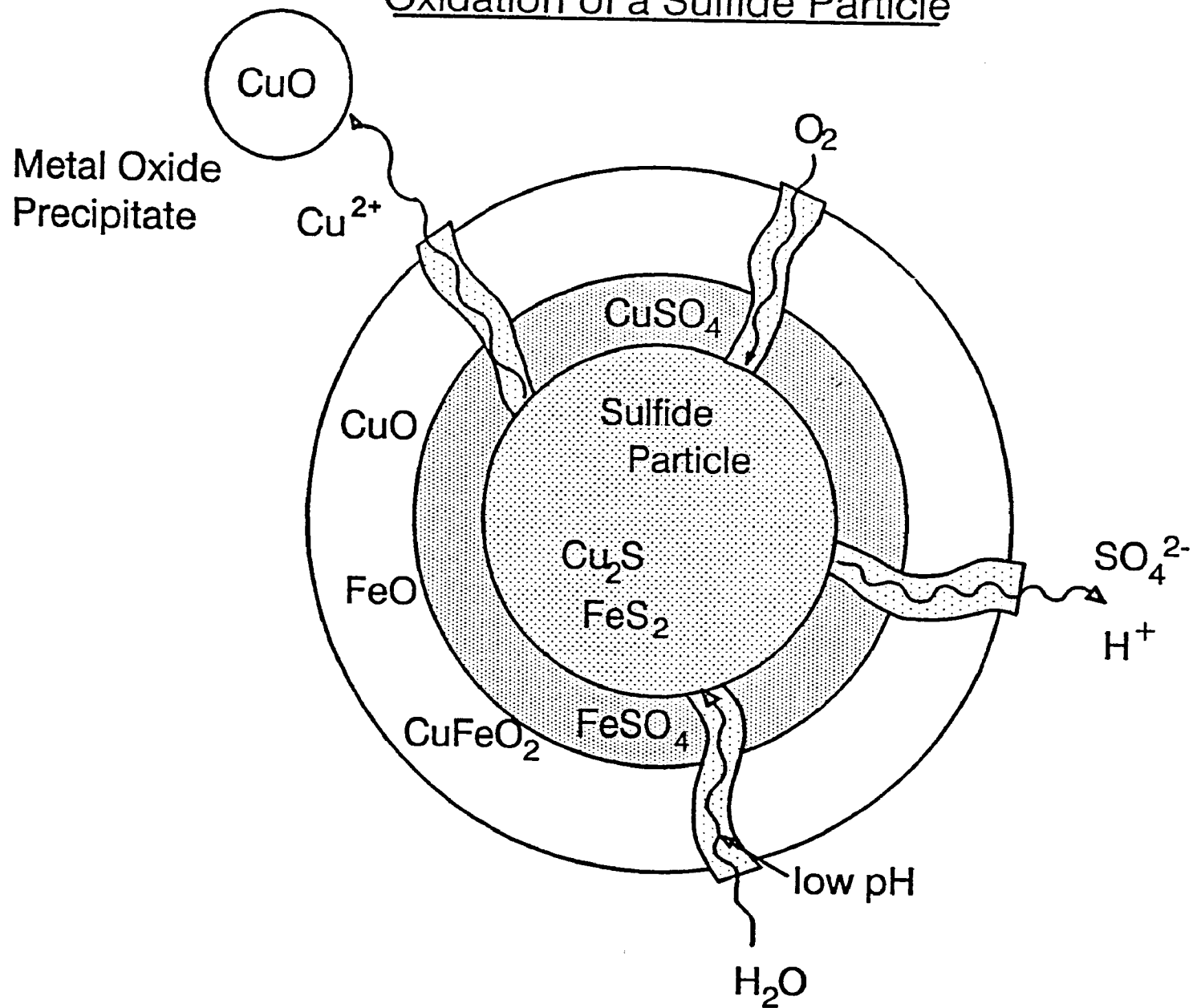
Oxidation Product Transport

As the sulfides are oxidized and byproducts (such as the sulfates, the oxides, 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 kinetically hinder

oxidation. Some oxidation products (H^+, SO_4^{2-}) will be removed faster than others (CuO, FeO), and so a buildup of some products (metal sulfates, oxides, and carbonates) occurs at the oxidation front between solid oxidized metal and metal sulfides. The buildup rate of this process 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 advection occurs during dry periods, so that the H^+ ion is trapped and increases the solubility of metal. Consequently, during dry periods, there is an increase in the source term for mobile and soluble metal outside the particles. During wet periods, pH at the particle surface is lowered 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.

In the groundwater away from the sulfide particle, pH drops, oxygen concentration increases, and the copper precipitates to form a metal oxide or carbonate colloid in suspension in the unsaturated zone. The groundwater around the sulfide particles has a lower hydrogen ion concentration than the water film around the sulfide particles, and the

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Oxidation of a Sulfide Particle

CuO

Metal Oxide
Precipitate

Cu^{2+}

O_2

CuSO$_4$

CuO

Sulfide
Particle

FeO

Cu_2S
FeS_2

SO_4^{2-}

H^+

CuFeO$_2$ FeSO$_4$

low pH

H_2O

higher pH reduces copper solubility relative to the water film. The higher pH will result in precipitates being formed in the groundwater, and these precipitates represent the bulk of the copper transported by leaching and runoff. An example of this will be shown later: pH is 4.5 in the unsaturated zone of the oxidized soil layer, but may be as low as 2.5 in the water film around the oxidizing sulfide particle. Copper will be carried in colloidal form into the rain runoff and into saturated groundwater.

Dependence of Geochemistry on Soil Depth

In the absence of a model that will define the geochemical conditions for a vertical soil core (1-D), the first step in the analysis of the waste site is to develop a general modeling framework. The soil core can be described as a mixture of tailings and alluvium 250 cm deep, 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).

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 soil core model corresponds to both measurements of depth vs. geochemistry in the Remedial Investigation Final Report (RIFR) and other literature on mine tailings geochemistry (Tetra Tech, 1986). Oxygen

diffusion to lower strata is limited by consumption in upper soil strata, particularly for tailings that are compacted and fine-grained, and 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)
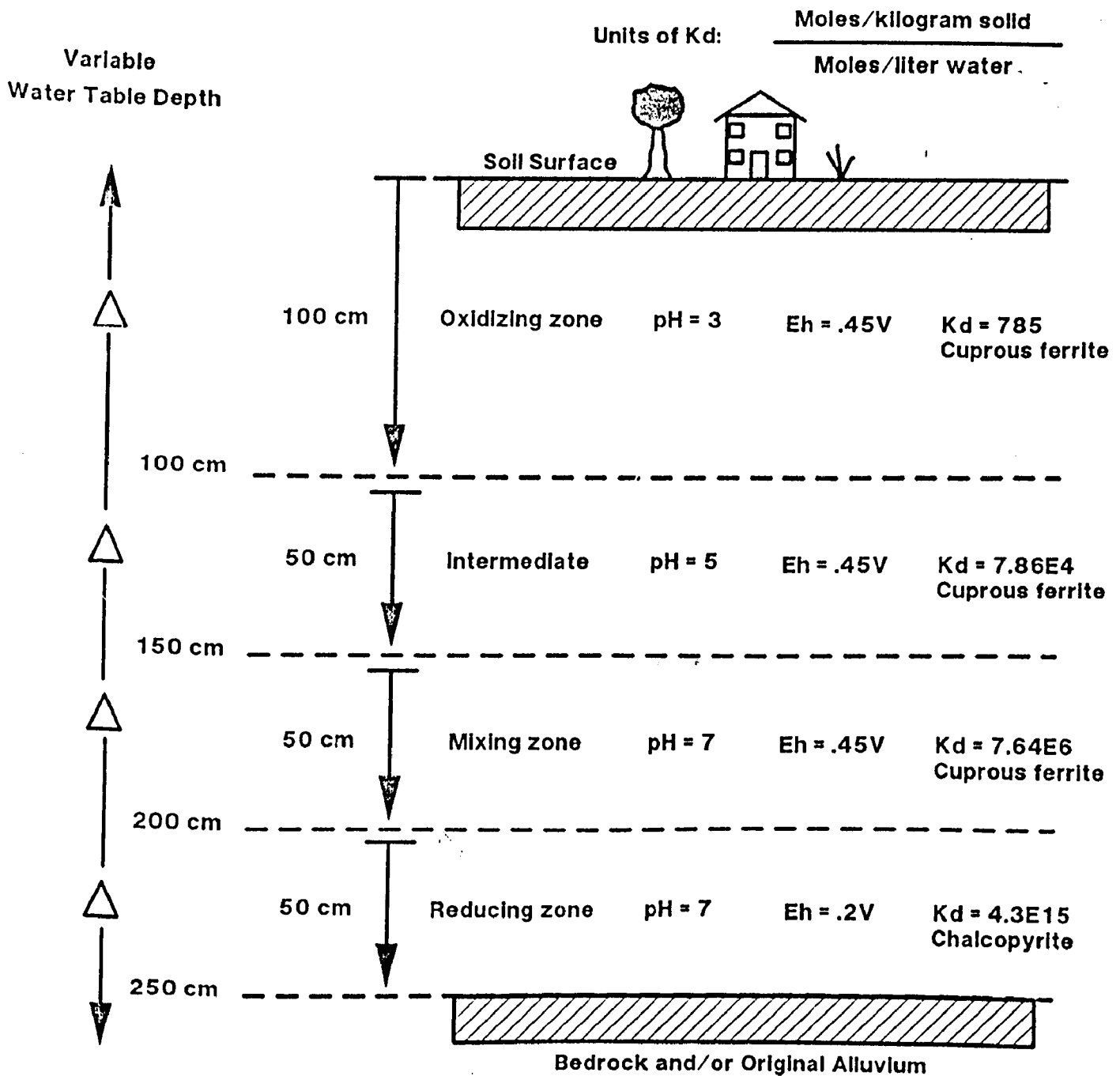
The conditions in the soil and tailings mixture are represented by two geochemical parameters: Eh (electrochemical potential) and pH (hydrogen ion abundance). In some cases the tailings have been mixed by alluvial or mechanical processes with the common associated bedrock of the Butte valley. This native bedrock has large portions of calcium carbonate that can neutralize acid produced by oxidation and corrosion of the sulfide particles.

The oxidized stratum in the unsaturated zone is the top layer, below which are, in sequence, the intermediate mixing layer, the mixing layer, and the reduced stratum. The top 100 cm of soil-tailings layer has excess oxygen available, and the Eh consequently is at an oxidizing potential of approximately 0.45V. Because of the rapid rate of hydrogen ion production, the pH in this layer is about 4.5.

The mixing layers have an electrochemical potential of 0.45V, and pHs of 5 and 7. The intermediate mixing layer is between 100 and 150 cm deep, with Eh=0.45V, and pH=5. The mixing layer is between 150 and 200 cm and has an Eh=0.45V and pH=7. In these layers, the
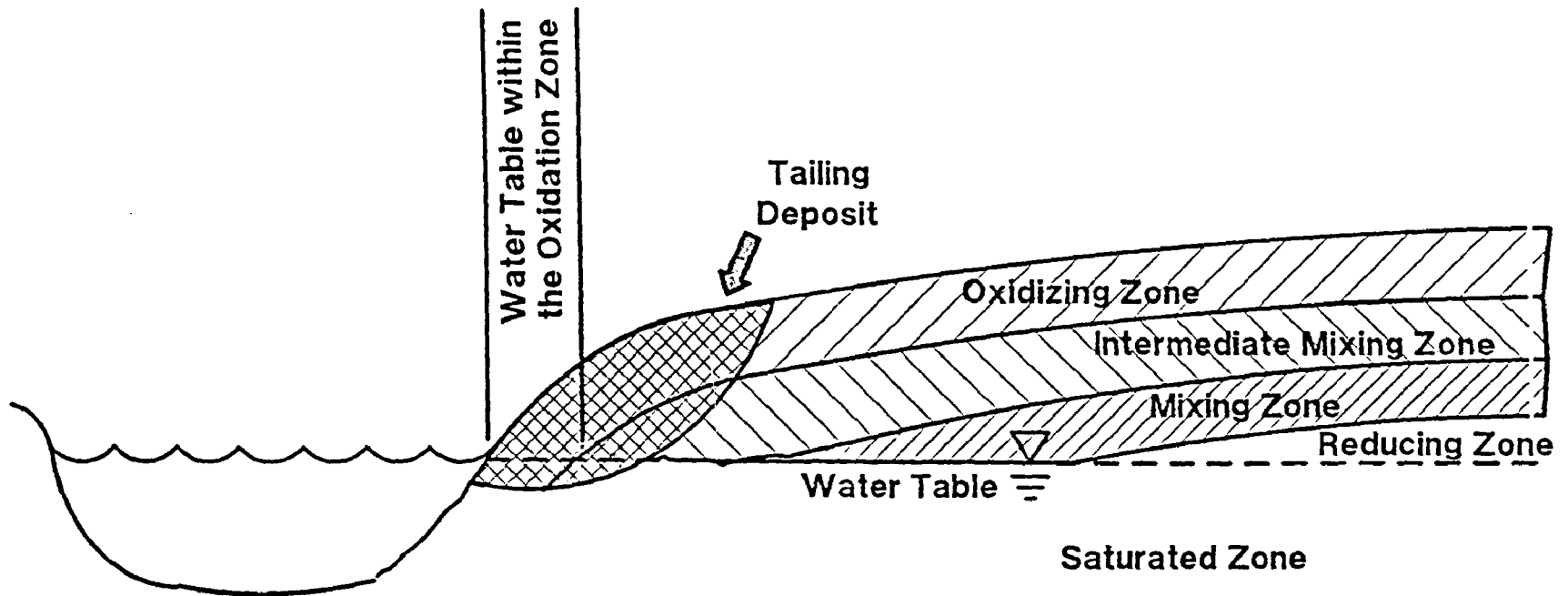
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FIGURE 4

Geochemical Profile
of the Unsaturated
Tailings and Alluvium

Units of Kd: $\dfrac{\text{Moles/kilogram solid}}{\text{Moles/liter water}}$

Variable
Water Table Depth

Soil Surface

| 100 cm | Oxidizing zone | pH = 3 | Eh = .45V | Kd = 785 Cuprous ferrite |

100 cm

| 50 cm | Intermediate | pH = 5 | Eh = .45V | Kd = 7.86E4 Cuprous ferrite |

150 cm

| 50 cm | Mixing zone | pH = 7 | Eh = .45V | Kd = 7.64E6 Cuprous ferrite |

200 cm

| 50 cm | Reducing zone | pH = 7 | Eh = .2V | Kd = 4.3E15 Chalcopyrite |

250 cm

Bedrock and/or Original Alluvium

Above diagram shows the geochemical
properties of the mixed tailings and alluvium
when they are above the saturated water level.

Profile of the River, Water Table, and Tailing Deposit

Water Table within the Oxidation Zone

Tailing Deposit

Oxidizing Zone

Intermediate Mixing Zone

Mixing Zone

Reducing Zone

Water Table

Saturated Zone

hydrogen ions mix with the reducing compounds in the soil core, but because some oxidation is still occurring, Eh remains at 0.45V. Oxidation can also occur by copper sulfate oxidizing iron sulfide to form copper sulfide and iron sulfate. Even in the presence of hydrogen ions from this layer and the oxidation layer above, the pH is higher, because of lower reaction rates and the neutralizing effect of the carbonates and the unoxidized sulfides.

In this idealized description of native soil and tailings, the bottom stratum is assumed to be a reduced layer, where there is a negligible concentration of oxygen. This layer is represented as having a reducing Eh of -0.2V.

The reduced soil layer has the least oxygen available and considerable reserves of reducing sulfide, so that both Eh and pH are in reducing ranges (Eh=-.2V, pH=7). Metal sulfates and sulfuric acid reaching this layer are precipitated and neutralized.

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 source term for copper in the oxidized stratum. The saturated zone is much better mixed than the unsaturated zone because of the continuous water phase.

Geochemistry Controls Leachate

Metal is mobilized by the hydrogen ions for transport into the unsaturated zone away from the sulfide particle surface to the groundwater and can then be carried to the surface water by runoff, erosion, or leaching.

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. If the saturated layer surface is adjacent to the reduced layer of soil and tailings, the model we have proposed will predict less 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).

A lower oxygen concentration causes a lower oxidation potential in the lower soil and tailings strata that receive leachate from the upper layers of the deposit, including sulfate ions, hydrogen ions, calcium, iron, and copper. The sulfuric acid may either be neutralized by calcium carbonate (calcareous bedrock and alluvium) or reduced by iron pyrite and other unoxidized sulfides.

To characterize the leachate that enters the water table, it is necessary to determine solubilities in the bottom unsaturated zone soil and tailings layer and the metal concentrations in the leachate in this layer. The geochemical

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conditions in the bottom 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).

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

The groundwater table can intercept any of the geochemical strata in the unsaturated zone, depending on the distance from the stream 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 shallower 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. (See Figure 4)

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. (See Figure 5)

Principal Models

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.

Metal Speciation Model—MINTEQA2

With MINTEQA2 the thermodynamic activities of all possible compounds in aqueous solution are solved for by the iterative reduction of 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 complex. The simultaneous equations are determined by the

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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 (Brown et al. 1987)

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 origin of flow in the unsaturated zone and on the tailing deposit surfaces may be from one or more of the following sources: overland flooding, infiltration, underflow, and runoff from the slopes above the stream bank. Rainfall is the major source of contribution to all of the above 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 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 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 capillary transport of contaminants to the surface from the subsurface and overland flood transport of metals. Capillary transport occurs when the soluble metal is carried to the surface of the soil by upward flow when evapotranpiration is occuring 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. Overland flood transport of metals is distinct from transport by overland flow erosion, and is similar to sediment transport in stream and rivers. (Figure 6)

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FIGURE 6

METAL LOADINGS
PATHWAYS
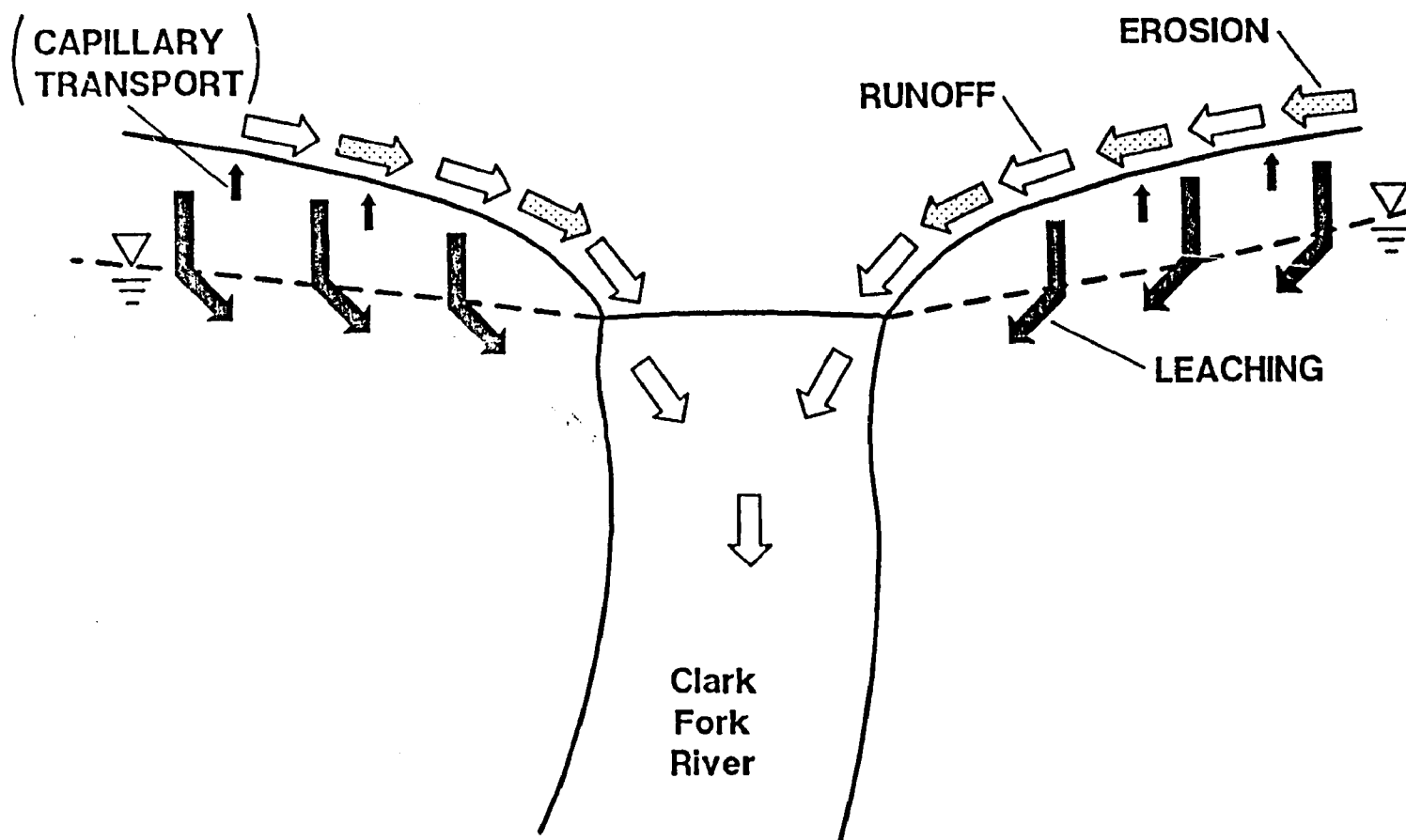
PRZM evaluates the magnitude of metals loading to the river for each of the three pathways.

PRZM includes a parameter describing the relative amount of contaminant in solid phase versus aqueous phase. This parameter is called the partition coefficient, and is predicted using a measured solid phase concentration of metal along with a soluble fraction of metal predicted with MINTEQA2.

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 (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 release 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 is 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 et. al. 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 nanometers 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 sidestream deposits and other sources; it adjusts the metals

Table 1

Waste Site Areas

Location	Area (hectares)	Type of wastes
Butte surface	1049	waste rock
Butte subsurface drainage	not applicable	acid mine
Anaconda	1500	smelter waste
streamside and alluvium	648	mixed tailings

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.

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 nanometers 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 nanometers to 1 nanometer) 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 contaminant 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 width of the tailings, hydraulic gradient, porosity, and hydraulic conductivity. Calculation of V is based on the width of the tailings, porosity, and the depth of the aquifer. Porous media flow is governed by Darcy's Law. 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 aquifer thickness is used to estimate the total flow through the aquifer. 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.

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 flow out of the aquifer and into the surface water is based upon calibrated groundwater velocities between 1.6 and 16.0 m/day. 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 waste deposit widths, which could be much larger for the off-stream sites in Anaconda and Butte. 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.

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 micrometers 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

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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 GCTRAN 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.

Removal of Metals in the Warm Spring Ponds in NPSOUT

The NPSOUT program performs the additional function of removing copper in the stream at the end of Segment 6 of the surface water model (that is, at the exit to Warm Springs Pond 3). The measured removal efficiency (mass removed/initial contaminant mass) of total copper (suspended and dissolved) between the inlet to Warms Springs Pond 3 and the outlet of Warm Springs Pond 2 is 80% on average. This removal efficiency does not have any apparent dependence on flow rate through the ponds. The apparent independence of removal rate efficiency from flow rate leads

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to the hypothesis that residence time for the metal in the liming/precipitation ponds does not affect removal efficiency, and that removal efficiency is constant. The approach taken in NPSOUT to account for removal of copper metal from the stream in the Warm Springs Ponds was to use NPSOUT to remove 80% of all copper loadings from stream loadings to surface water segments 1 through 6.

The quantity and characteristics of available sediments affect transport, removal, storage, and release of heavy metals. Adsorption parameters and sediment/eroded soil particle size distributions are not currently available. The nonpoint source sediment loads are included in PRZM output; sediment data are provided to the WASP4 model as a nonpoint source from the erosion of the stream banks. The model results indicate that the sediment transport is less than 5% of the metals transported.

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 (1988, 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.

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, 1987); therefore, the main stream segmentation was chosen to coincide with the measurement stations of that study as outlined in Table 2. The surface water modeling results are compared to data from the RIFR and from the Montana Water Quality Bureau.

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 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.

Application of the simplified surface water transport model WASP4 results in a metal concentration time series for each surface water segment.

Results and Discussion

Surface Water Modeling Results

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 and the Anaconda smelter with the other subsites for Segment 7. Each subsite has a distribution coefficient Kd, and a parameter Q/V.

Second, the in-stream copper concentration predictions for the Upper Clark Fork River basin from this modeling framework are compared to measured surface water concentrations. The comparison is examined for conclusions about the modeling system and the assumptions used, and for observations about the approach.

Results of Tributary and Main Dump Sites

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 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

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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

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 were performed with NPSOUT, and the results are compared with a selection of 15 measurements that date from 1984 through 1986 (Bahls 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 7 through 10) 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 10 and 11 demonstrate the results of a change in the Q/V ratio (called TQDIVV in the model) for the off-stream 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.

The type of groundwater transport and mixing model used strongly affects the predicted loadings of metal into the surface water. Changes in the mixing model to include more than one mixing volume might be appropriate. The efficiency of mixing in the model also might be changed in order to improve

the model. Only the rate of flow was varied in the model (Q/V parameter) as applied to date.

The PRZM model results reveal that the allocation of metal is dependent on the partition coefficient K_d. Partition coefficient may vary 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 7, 9, and 12 compare surface water copper concentrations with concentration predictions for several values of K_d.

In-Stream Predictions

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 13 through 16 below show the model predictions for the above scenarios.

The normal flows for spring and winter also were examined. Finally, the low flow period during late summer and the fall were examined (see Figure 17). Without having experimental data for comparison, one can nonetheless see the severity of high copper concentration in the stream during low flow periods.
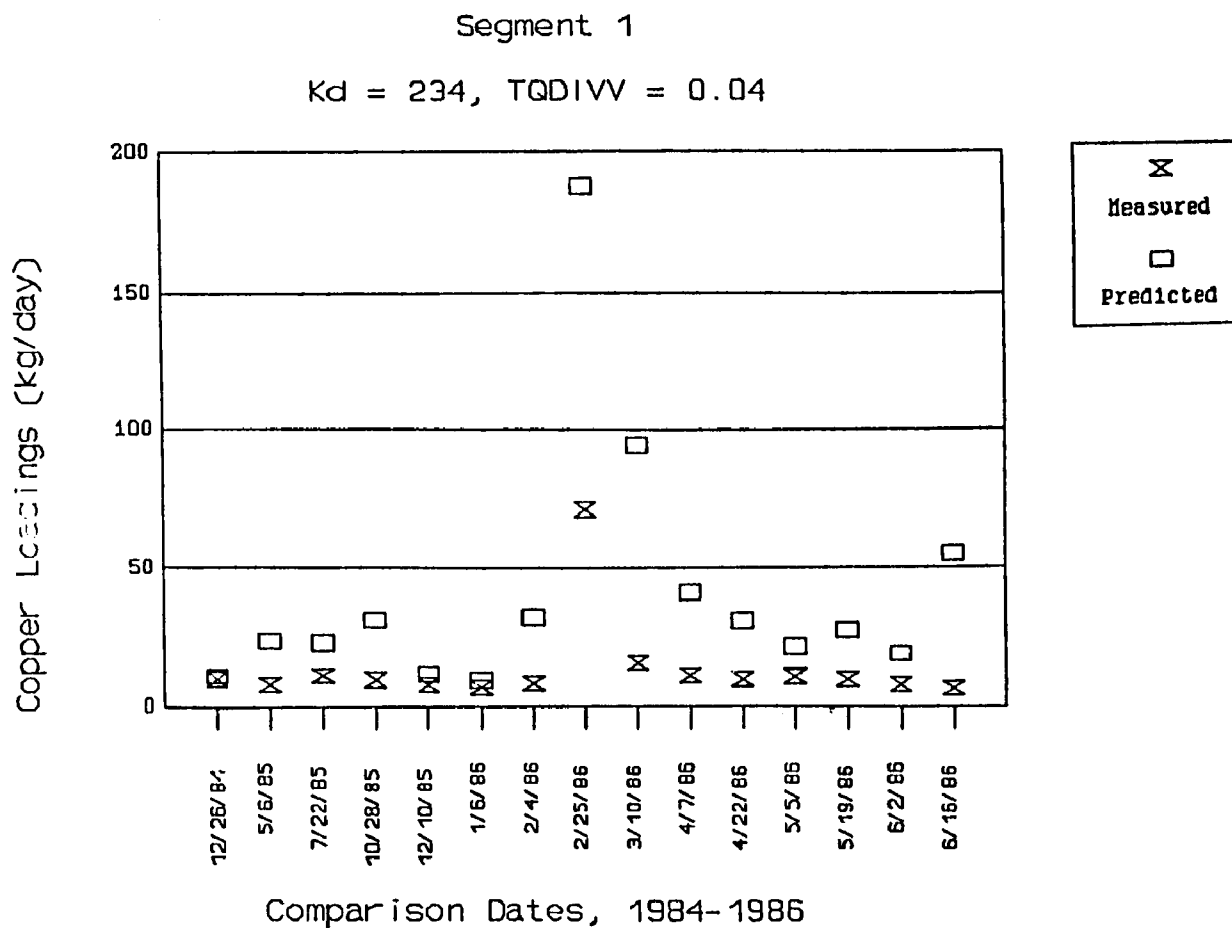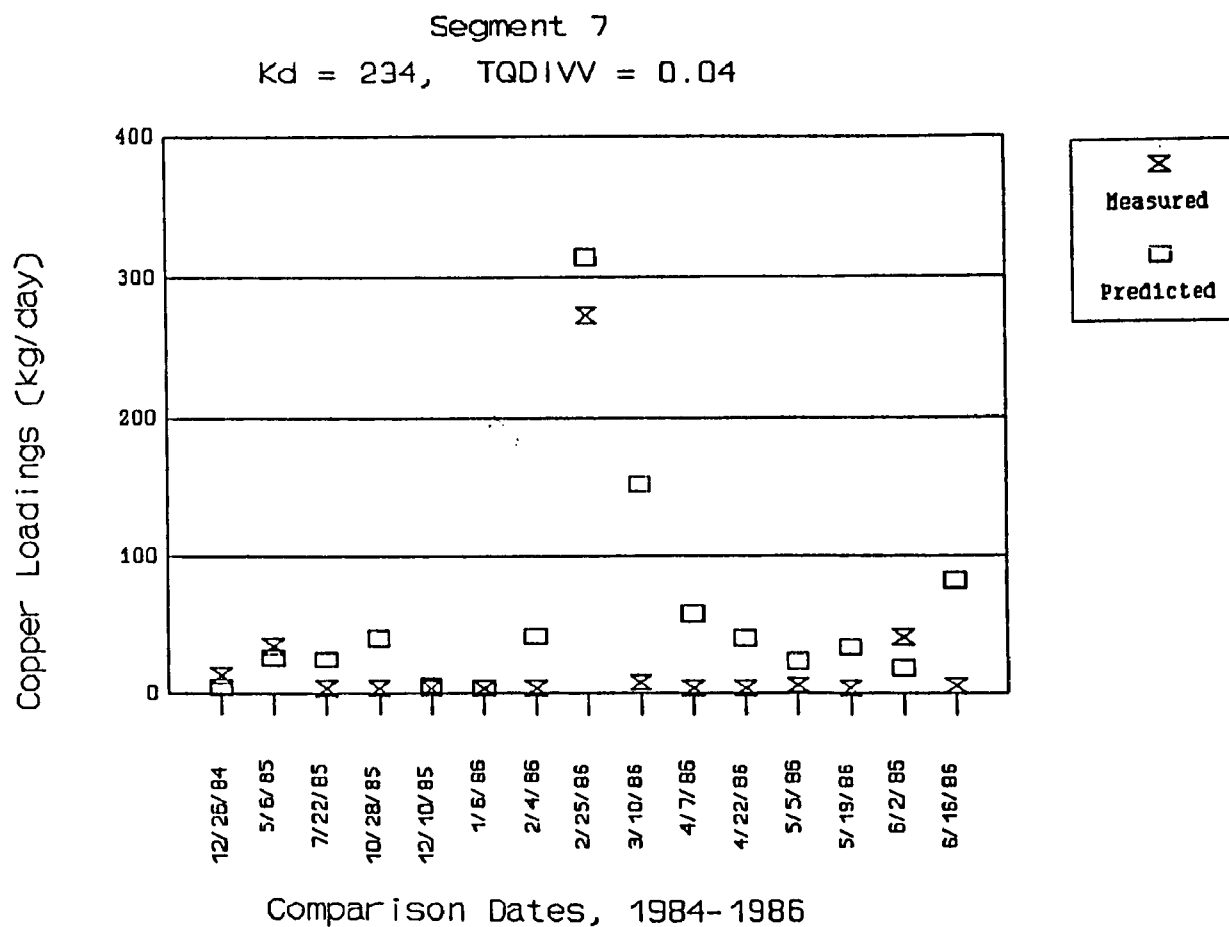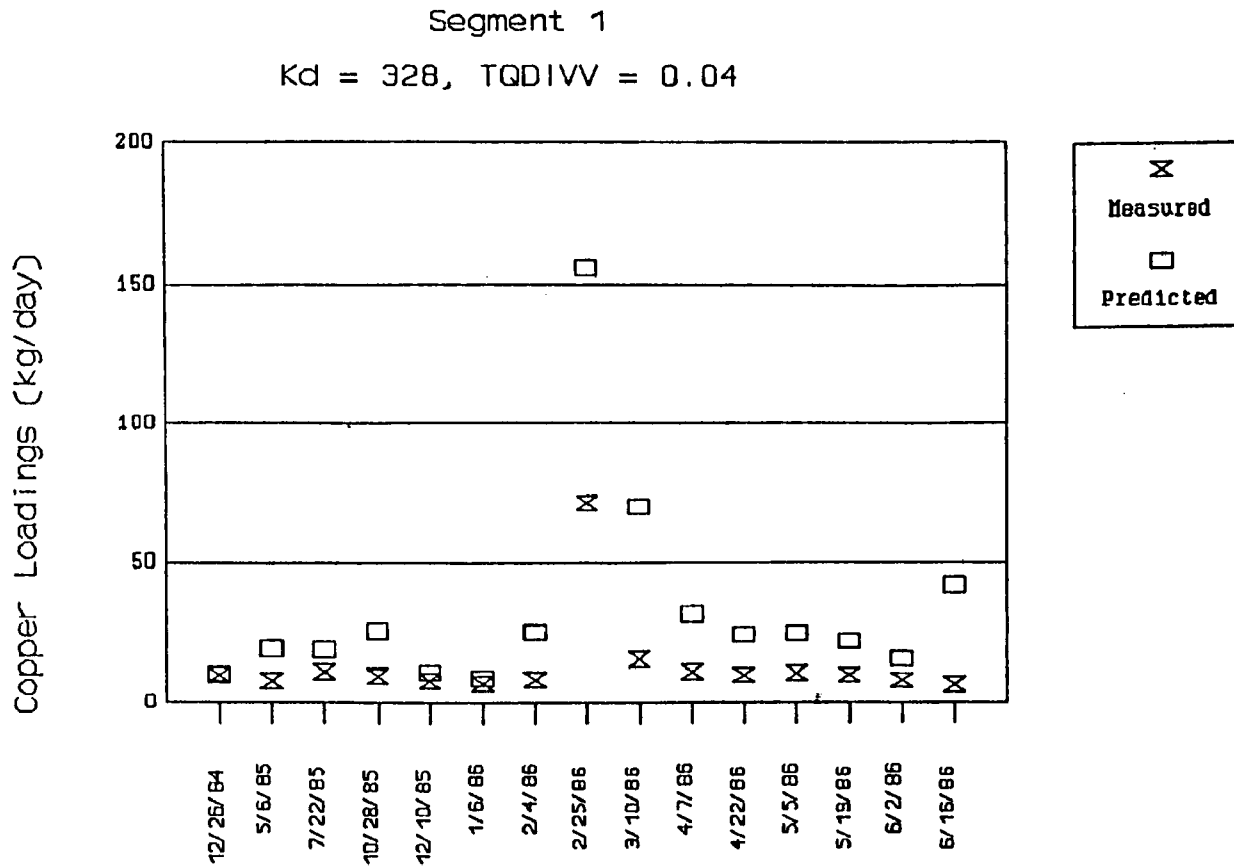
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FIGURE 7

Segment 1

Kd = 234, TQDIVV = 0.04

Figure 7. Predicted vs.Measured Copper Loadings

FIGURE 8

Figure 8. Measured vs. Predicted Copper Loadings

FIGURE 9

Segment 1

Kd = 328, TQDIVV = 0.04

Figure 9. Measured vs. Predicted Copper Loadings
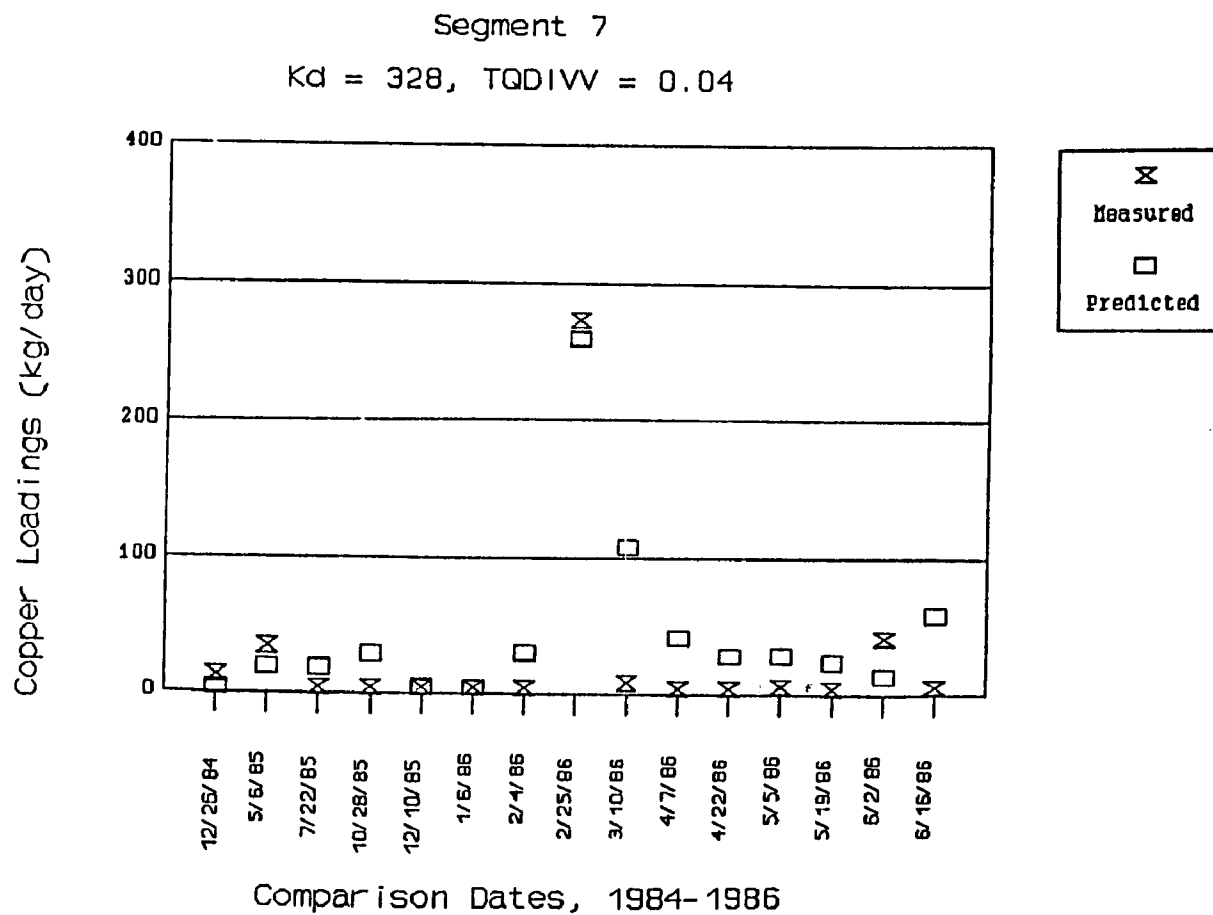
FIGURE 10

Segment 7

Kd = 328, TQDIVV = 0.04
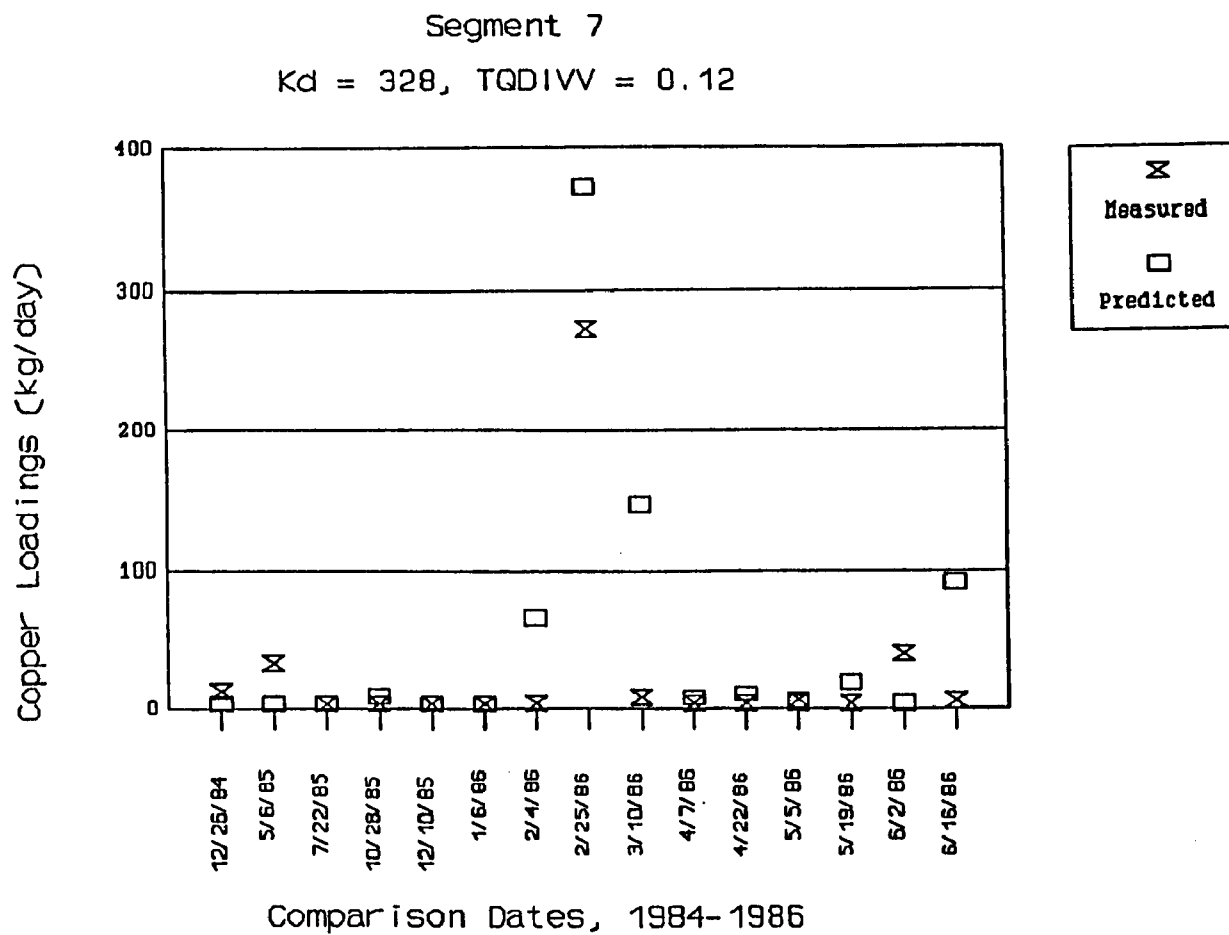

Figure10. Measured vs. Predicted Copper Loadings

FIGURE   11

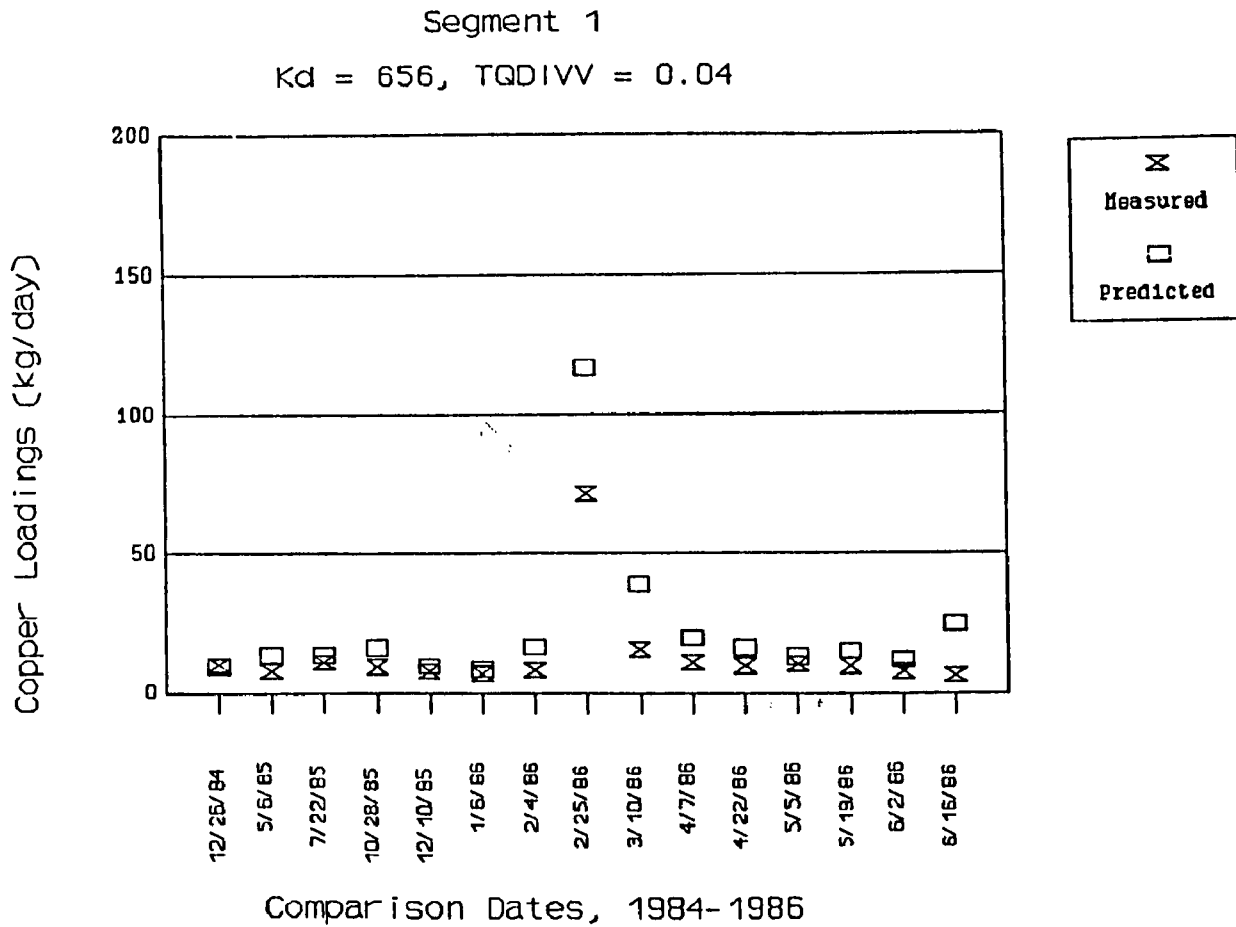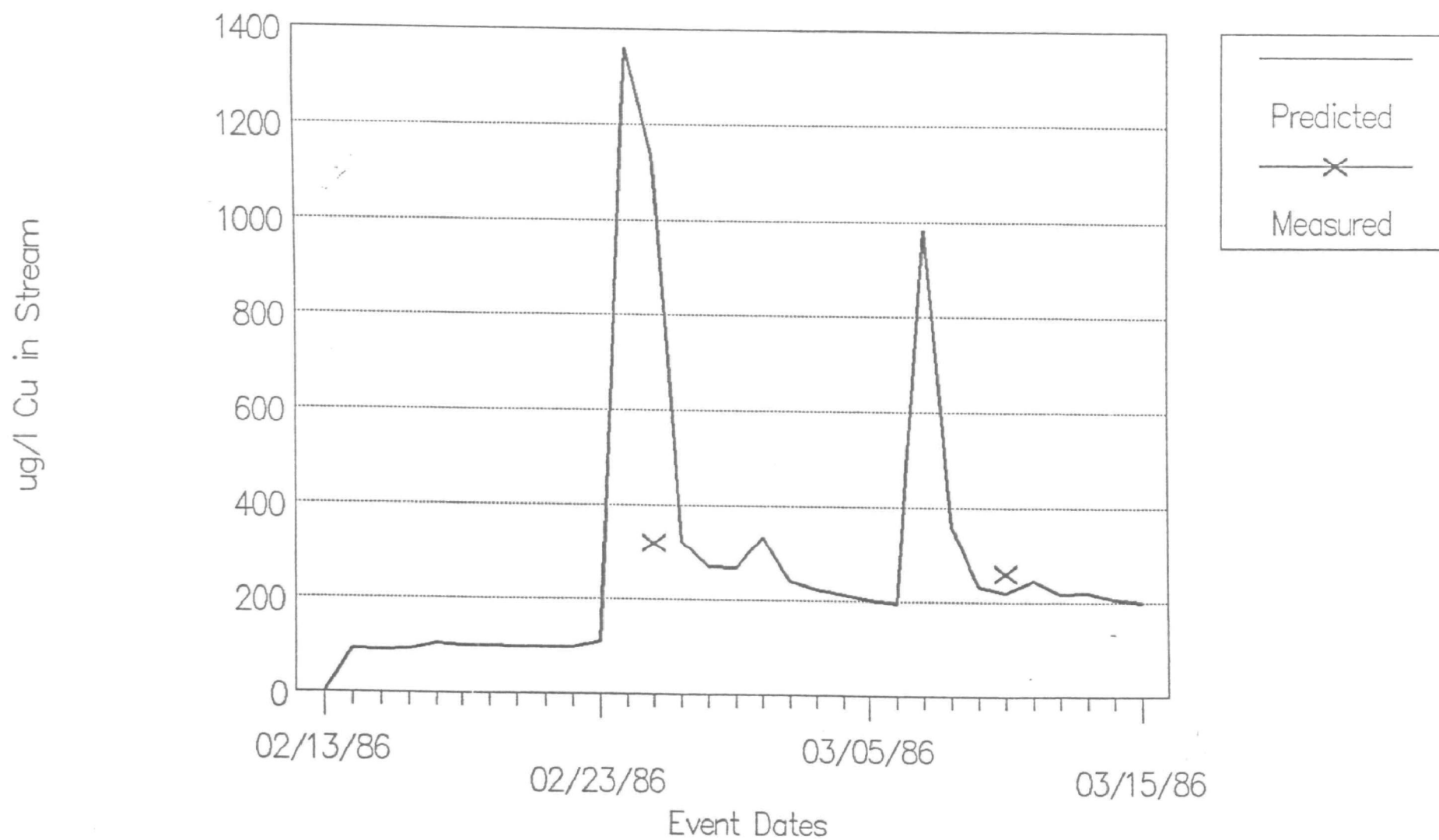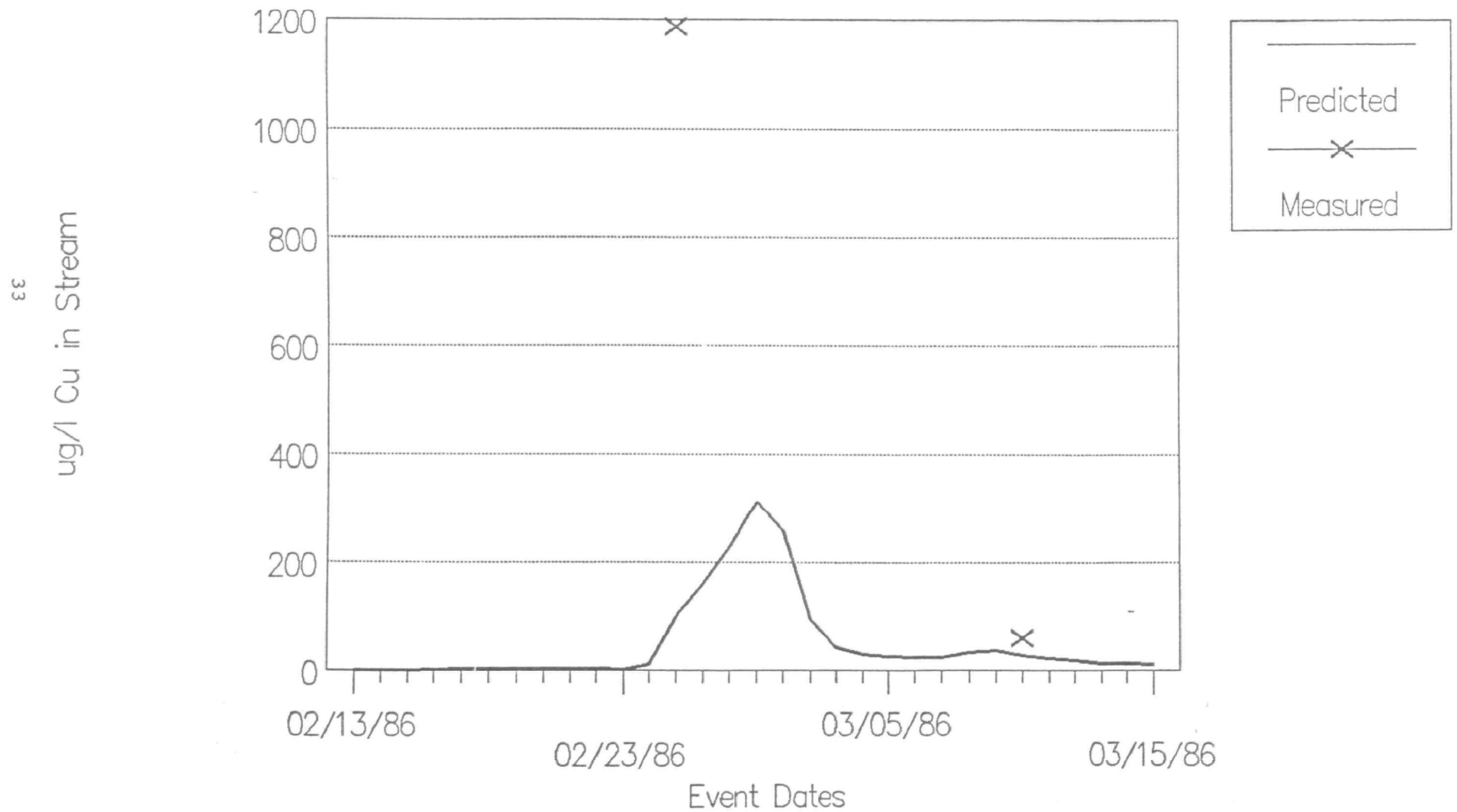Figure 11.   Measured vs. Predicted Copper Loadings

FIGURE 12

Segment 1

Kd = 656, TQDIVV = 0.04

Figure 12. Measured vs. Predicted Copper Loadings
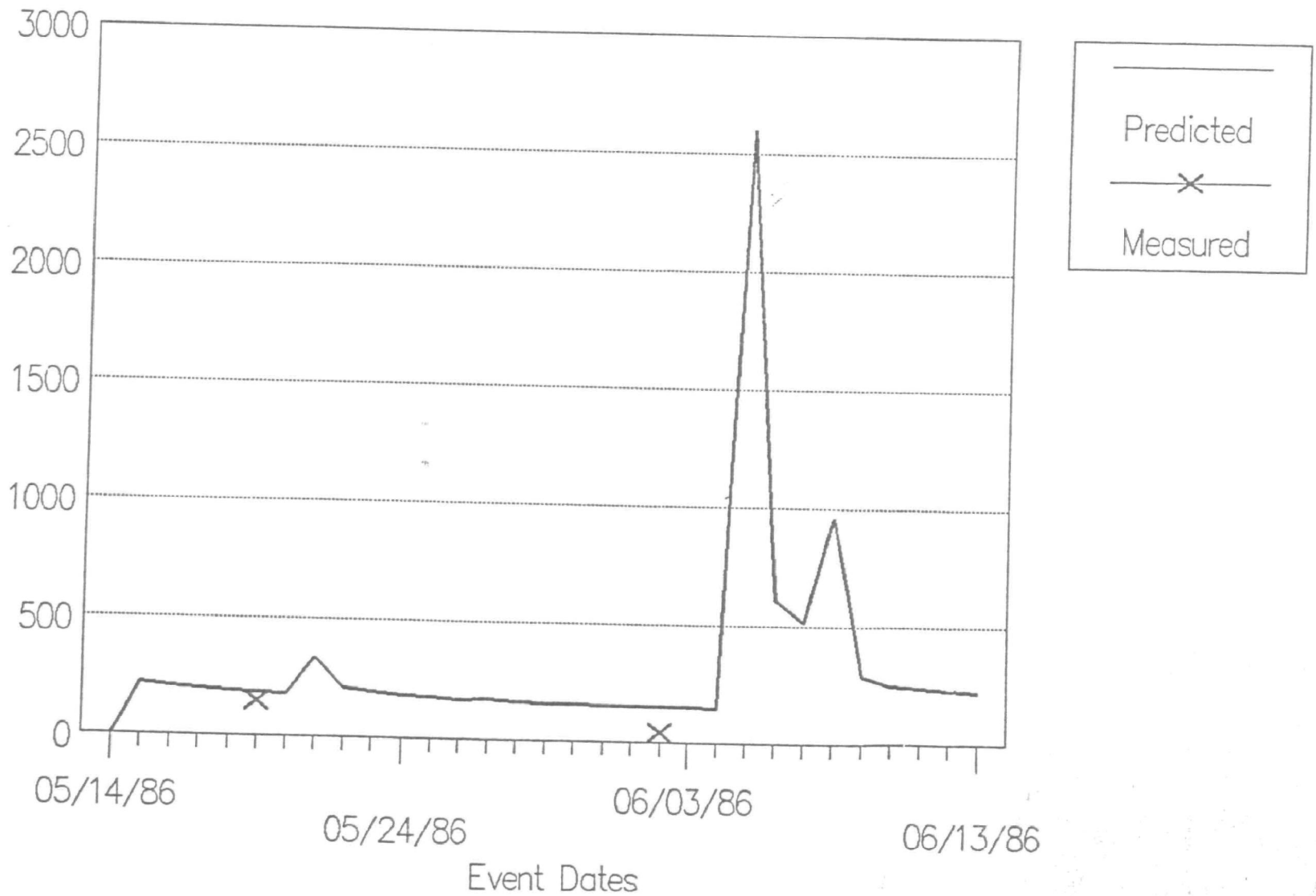
Winter Flood

Segment 1 Predicted, Measured

ug/l Cu in Stream

Event Dates

Legend:
- Predicted
- × Measured

Winter Flood
Segment 11 Predicted, Measured

Spring Flood
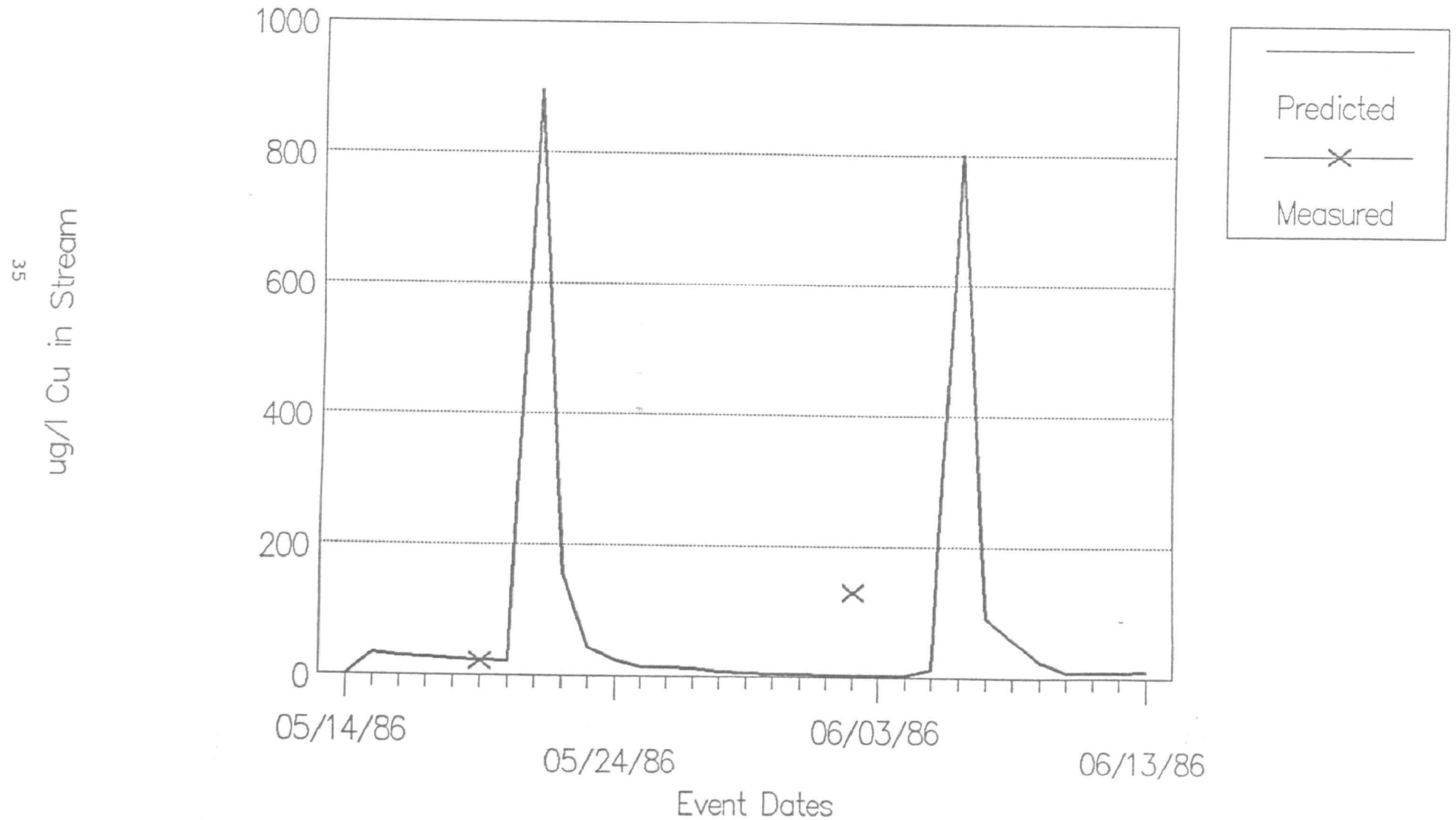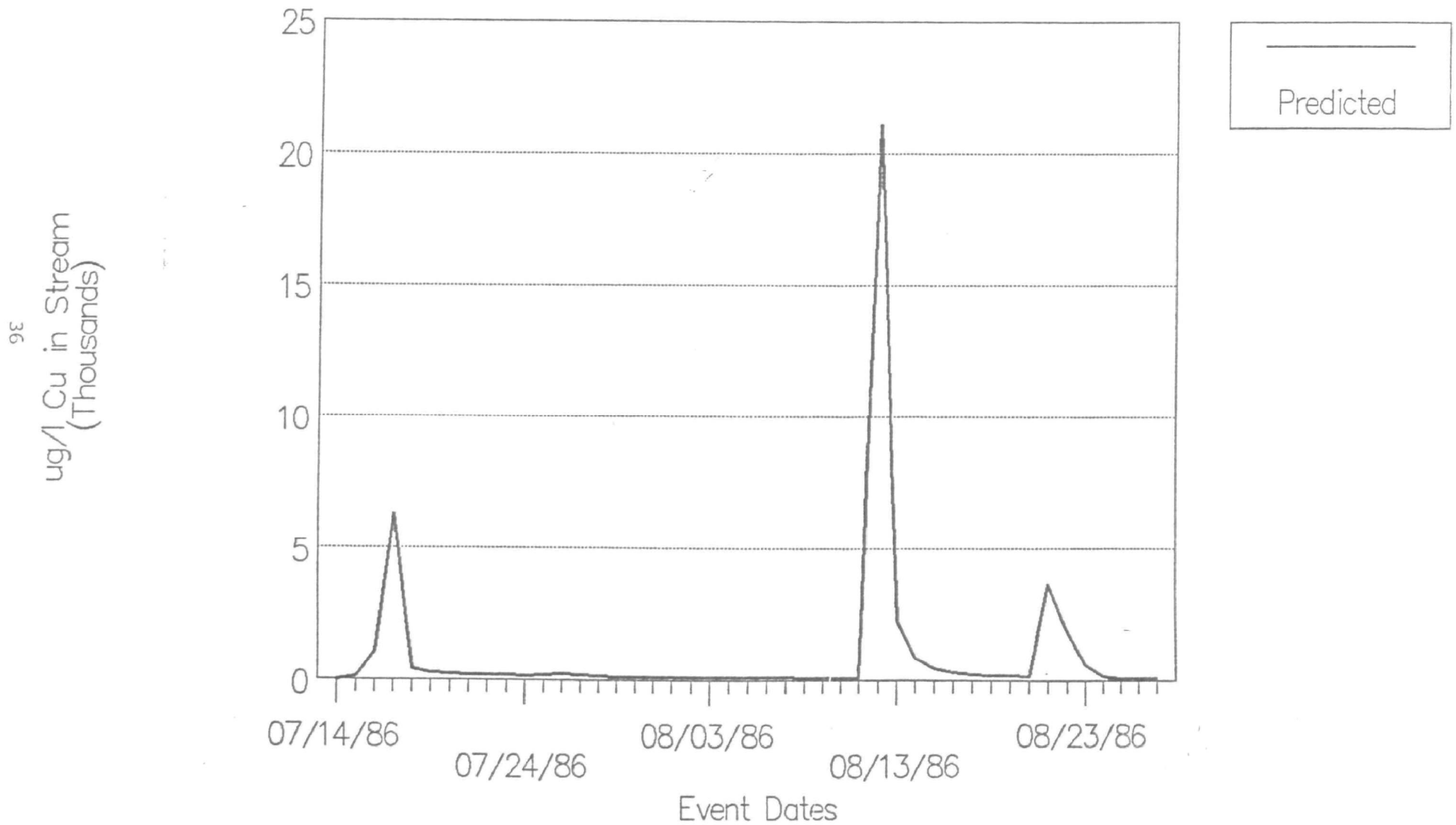# Segment 1 Predicted, Measured

Spring Flood
Segment 11 Predicted, Measured

Normal Fall Flow
Segment 7 Predicted, Measured

Conclusions

The variance between the measured winter flood concentrations in the Upper Clark Fork River and the predictions using the methods and models depicted 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 during floods before the Warm Springs treatment ponds were constructed. The outflows from the Warm Springs Ponds are accurately predicted. Resuspension of sediments in the ponds is accounted for with the metal removal efficiencies. During a flood, resuspension of stream-bed contaminant may be the primary contaminant source if flows have sufficient power to strip the armored cobble bottom of the river and resuspend sediments.

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 sidestream contaminant sources may improve the predictive capability of this modeling system.

For the winter flood, 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 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 for such cases may be necessary.

The goal of improving prediction of contaminant transport raises the need for a 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 in immobile solids. Having an accepted and reviewed linkage would be a great advantage on any other project where the transport and flow in a saturated zone or in a variably porous and conductive subsurface controls the contaminant release.

Finally, we 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 components such as heavy metals, sulfates, metal-bearing colloids, and sediments.

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