SPATIAL AND TEMPORAL TRENDS OF TRACE METALS IN SURFACE WATER, BED SEDIMENT, AND BIOTA OF THE UPPER CLARK FORK BASIN, MONTANA, 1985-95.

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ABSTRACT

This report describes the hydrologic characteristics of the upper Clark Fork basin during 1985-95, and the spatial distributions and temporal trends of metals in surface water, bed sediment, and biota. The parameters evaluated include streamflow, annual suspended-sediment and metal loads, metal concentrations in fine-grained and bulk bed sediments, and metal concentrations in a widely-distributed species of aquatic insect, *Hydropsyche cockerelli* (Trichoptera). The most important results of this study characterize aspects of the variability in these different indicators of metal exposure. The current analysis also is an initial attempt to characterize and compare conditions between the period before remediation (1985-90) and after several remedial treatments in the upper reach of the basin (1991-95).

Both metal loads and metal concentrations in insects and bed sediment follow a persistent spatial gradient in the Clark Fork, with many features consistent among measures. The four major tributaries located between Warm Springs Ponds and Turah Bridge (Warm Springs Creek, Little Blackfoot River, Flint Creek, and Rock Creek) contributed only a minor proportion of the total metal discharged to Milltown Reservoir. Concentrations of metals in fine-grained bed sediment and in insects are also low in most of the tributaries, compared to the Clark Fork. The highest concentrations of metals in the monitoring network occur in Silver Bow Creek, upstream of the Warm Springs Ponds. Metal concentrations are significantly reduced immediately below the outfall of the Warm Springs Ponds. The largest single contribution to the cumulative metal load entering Milltown Reservoir was from the 39.9 km reach between the Clark Fork near Galen and the Clark Fork at Deer Lodge. This is also the reach of the Clark Fork with the highest metal concentrations in bed sediment and insects.

Streamflow has a large influence on year-to-year variability of suspended-sediment and metals transport, and on metal concentrations in insects and probably bed sediment. However, the influences are complex, site-specific, and reach-specific. Comparisons of conditions between 1985-90 vs. 1991-95 were affected by year-to-year hydrologic variability. Detection of future trends will require examining hydrologic conditions concurrently with metal transport and other indicators of metal exposure, understanding year-to-year differences in concentrations and transport, and coordination of surface water, bed-sediment, and biota sampling, especially in the highly variable upstream reach of the river. Trend detection will become more sensitive as variability in the system is better understood.

INTRODUCTION

Background

The Clark Fork of the Columbia River, which drains western Montana, originates at the confluence of Silver Bow Creek and Warm Springs Creek (fig. 1). Mining, milling, and smelting of metal ores began in the 1850's in the headwaters of the Clark Fork, and for more than a century, large quantities of waste rock, tailings, and slag (hereafter referred to as tailings) rich in heavy metals were produced. Andrews (1987) estimated that 100 million tons of tailings was supplied to the Clark Fork during the period of mining from 1880 to 1982. Erosion and runoff have transported and dispersed tailings along the Clark Fork mainstem, and extensive metal-enriched deposits occur in the floodplain, especially in the upper 100 km where slickens (unvegetated tailings deposits) are present (Moore and Luoma, 1990; Nimick and Moore, 1994). Many of the mining and tailings-disposal practices that contributed to the greatest dispersion of tailings have been discontinued, as have many smaller-scale mining operations in tributary basins throughout the basin. However, metal enrichment remains evident in Clark Fork sediments and biota over hundreds of kilometers of the river (Andrews, 1987; Moore and Luoma, 1990; Axtmann and Luoma, 1991). Metals in the Clark Fork, primarily Cu, historically have caused fish kills and suppression of fish production (Phillips, 1985). Silver Bow Creek and the Clark Fork mainstem from Butte to Milltown Reservoir were designated a Superfund Site by the U. S. Environmental Protection Agency (USEPA), as a result of potential risks to aquatic life and human health from exposure to elevated metal concentrations.

Efforts to decrease the amount of tailings discharged directly into the river began in 1911, when settling ponds were first constructed (fig. 1). The last of the three ponds was completed in the 1950's. Although these ponds capture substantial amounts of tailings, metal-rich sediments continue to move through the river system, probably originating from floodplain deposits below the Warm Springs Ponds and, until recently, from tailings along a channel that bypassed the ponds due to insufficient storage capacity (Phillips, 1985). Remediation efforts were initiated in 1988 as part of the Superfund cleanup process and now include projects on parts of Silver Bow Creek, Warm Springs Creek, and the reach of the Clark Fork above Deer Lodge (Montana Superfund Sites Status Report--1994, written communication, USEPA, 1995).

Remediation activities undertaken thus far are designed to lower risks to human health and biota by reducing metal exposure. The term "remediation" as used in this report does not imply the final course of actions taken to clean up metal sources. Rather, the term is used to refer to the initial treatments (described in a subsequent section) implemented to mitigate some of the most acute sources of metal inputs in a limited area of the upper basin.

Major fish kills, which historically happened during some summer thunderstorms, have not been evident in recent years since the initial remediation treatments. Of continuing concern, however, is the potential effect of chronic toxicity on biota from metal-enriched sediments already in the river and the ongoing erosion and transport of dissolved and particulate metals from the extensive channel and floodplain sources in the valley. The effectiveness of the remediation efforts in reducing downstream contamination from these sources is not well known, but long-term monitoring is being conducted to identify and evaluate changes over time (Lambing and others, 1994).

Purpose and Scope

This report describes the hydrologic characteristics of the Clark Fork and the spatial distribution and temporal trends of metals in surface water, bed sediment, and biota in the upper Clark Fork basin between 1985 and 1995. Selected metal data for these three media were chosen to provide several independent environmental indicators of metal concentrations in the river and changes in metal enrichment over time. Correlations among the different indicators, such as metal loads in water, metal concentrations in bed sediment, and metal concentrations in tissues of aquatic insect larvae, are used to evaluate factors that might influence metal bioaccumulation and bioavailability.

Data from the integrated monitoring network have been used to quantify the transport of metals in the river and qualitatively assess the possible effect of remediation on trends in metal concentrations in bed sediment and aquatic insects. Although the integrated monitoring network has only been in place since 1993, some comparable data for the period 1986-1992 were collected at the same sites as the monitoring network, by independent programs. The long-term data set allows for examination of metal trends in bed sediment and biota relative to naturally-varying hydrologic conditions and implementation of remediation efforts.

Data used in this report are restricted to selected data collected by the USGS from 1985-95 (table 1). The mainstem study area of the Clark Fork extends from Silver Bow Creek at Opportunity to the Clark Fork below the confluence of the Bitterroot River (fig. 1). The major emphasis of this report is placed on sites above Milltown Reservoir.

Water-quality and transport characteristics for the period 1985-90 are described by Lambing (1991). Data from the additional sites added to the network in 1993 are included in the transport analysis reported here to describe transport characteristics for the period 1991-95. Metal transport in surface water and suspended sediment is described for Cu, Pb, and Zn. These metals were chosen because of their potential toxicity to aquatic biota and because total-recoverable concentrations in surface waters were sufficiently above analytical detection limits to allow calculations of metal loads. Cadmium is not included in transport analysis because low concentrations in surface water, commonly below detection limits, preclude load computations. Streamflow and suspended-sediment transport are also examined because of their strong relationship to metal transport.

Metal concentrations in bed sediment and aquatic insects are described for Cd and Cu for 1986-95. The two metals were evaluated for trends because both are potentially toxic to aquatic biota and, geochemically, they behave similarly to a variety of metals. Samples were collected from a variety of sites over this period, but most of the data in this report are restricted to network sites (table 1).

Interpretations of bioaccumulation data are restricted to one species, the net-spinning, omnivorous, filter-feeding caddisfly *Hydropsyche cockerelli*. *H. cockerelli* is relatively metal tolerant as evidenced by its widespread distribution in the Clark Fork basin; it is consequently an important food-chain organism for fish in both the mainstem and tributaries. Understanding trends in metal concentrations in tissues of a dominant aquatic insect species could be a valuable indicator of changes in sustained metal exposure to biota. Metal bioaccumulation in aquatic insects, including *H. cockerelli*, was described by Cain and others, (1992; 1995), and Axtmann and others, (1997).

Table 1. Type and period of data collection at long-term sampling stations in the upper Clark Fork Basin, Montana. Periodic water quality consist of onsite measurem physical properties and laboratory analyses of major ions, trace elements and suspended sediment. Prior to March 1993, laboratory analyses included only trace elements and suspended sediment, with the exception of Clark Fork below Missoula. Laboratory analyses of trace elements were made for fine-grained and bulk bed sediment, and biota.

Station Number	Station Name	River mi	River Km	Continuous record streamflow	Periodic water quality	Daily suspended sediment	Fine-grained bed sediment	Bulk bed sediment	Biota
12323600	Silver Bow Creek at Opportunity	-8.6	-13.8	07/88-09/95	03/93-09/95	03/93-09/95	07/92-08/95	08/93-08/95	07/92. 08/94-08/95
12323750	Silver Bow Creek at Warm Springs	-1.3	-2.1	03/72-09/79, 04/93-09/95	03/93-09/95	04/93-09/95	07/92-08/95	08/93, 08/95	07/92-08/95
12323770	Warm Springs Creek at Warm Springs	0	0	10/83-09/95	03/93-09/95	--	08/95	08/95	08/95
12323800	Clark Fork near Galen	2.9	4.7	07/88-09/95	07/88-09/95	--	08/87, 08/91-08/95	08/93-08/95	08/87, 08/91-08-95
12324200	Clark Fork at Deer Lodge*	27.7	44.6	10/78-09/95	03/85-09/95	03/85-08/86, 04/87-09/95	08/86-08/87, 08/90-09/95	08/93-08/95	08/86-08/87, 08/90-08/95
12324590	Little Blackfoot River near Garrison	36.9	59.4	10/72-09/95	03/85-09/95	--	08/86-08/87, 08/94	08/94	08/87, 08/94
12324680	Clark Fork at Goldcreek**	53.2	85.6	10/77-09/95	03/93-09/95	--	08/86-08/87, 08/90-08/95	08/93-8/95	08/86-08/87. 08/90-08/95
12331500	Flint Creek near Drummond	70.9	114.1	08/90-09/95	03/85-09/95	--	08/86, 08/89, 07/92-08/95	08/93-08/95	08/86, 07/92-08/95
12331800	Clark Fork near Drummond***	84.5	136	04/93-09/95	03/93-09/95	--	08/86-08/87, 08/91-08/95	08/93-08/95	08/86-08/87. 08/91-08/95
12334510	Rock Creek near Clinton	106.5	171.4	10/72-09/95	03/85-09/95	--	08/86-08/87, 08/89, 08/91-08/95	08/93-08/95	08/87, 08/91-08/95
12334550	Clark Fork at Turah Bridge, near Bonner	117.9	189.7	03/85-09/95	03/85-09/95	03/85-09/95	08/86, 08/91-08/95	08/93-08/95	08/86, 08/91-08/95
12340000	Blackfoot River near Bonner	123.3	198.4	10/39-09/95	03/85-09/95	07/86-03/87, 06/88-09/95	08/86-08/87, 08/91, 08/93-08/95	08/93-08/94	08/86-08/87, 08/91, 08/93
12340500	Clark Fork above Missoula	126.3	203.2	03/29-09/95	07/86-09/95	07/86-03/87, 06/88-09/95	--	--	--
12353000	Clark Fork below Missoula+	138.4	227.7	10/29-09/95	++10/78-09/95	--	08/86, 08/90-08/95	08/93-08/95	08/86, 08/90-08/95

*Bed sediment and biota sampled 4 Km upstream from water-quality station in 1986-87, and 1990-91.
**Bed sediment and biota sampled 4 Km upstream from water-quality station in 1986-87, and 1990-91
***Bed sediment and biota sampled 5.5 km downstream from water-quality station to conform to previous sampling location.
+Bed sediment and biota sampled 48.3 Km downstream from water-quality station to conform to previous sampling location.
++Water quality sampled as part of a separate program; parameters analyzed modified in 1993 to conform to long-term program.

Previous Investigations

The Clark Fork has been the subject of numerous studies of the distribution, movement, and biological effects of metals (Nimick and Moore, 1991; Lambing, 1991; Cain and others, 1992; Nimick and Moore, 1994; Woodward and others, 1995; Phillips and Lipton, 1995). For example, Andrews (1987), Brooks and Moore (1989), and Axtmann and Luoma (1991) reported a downstream decrease of metal concentrations in bed sediment, with the highest concentrations of cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) in the upper reach of the river, and exponentially decreasing concentrations with distance downstream. Cain and others, (1992) described a similar decreasing downstream gradient in metal concentrations of benthic insects. Lambing (1991) determined that the highest metal loads per river kilometer occurred in the reaches between Galen and Deer Lodge during 1985-90. Low diversity of insect communities also is evident in this reach (McGuire, 1988, 1995) . Food-chain transfer of metals from insects to trout in the upper reach has been demonstrated (Woodward and others, 1995), as have adverse effects of the metal-rich environment on fish (Marr and others, 1995).

Metal concentrations in surface water, bed sediment, and aquatic insects of the Clark Fork and some of its tributaries have been monitored by the U. S. Geological Survey (USGS) since 1985. A sampling network for surface water was established for six sites in 1985 in the upper Clark Fork basin above Milltown Reservoir. Additional sites were added on the Clark Fork mainstem above Missoula in 1986 and near Galen in 1988. The network was expanded in 1993 to include 14 sites between Silver Bow Creek at Opportunity and the Clark Fork below Missoula (fig. 1). The Clark Fork below Missoula site had been operated as part of a separate, national water-quality program since 1978. Sampling of bed sediments and aquatic insects was conducted intermittently at a variety of sites between 1986 and 1992 as part of an independent USGS research project. In 1993, the bed sediment and biological sampling sites were integrated with the surface-water sites to establish a basinwide network for systematic, long-term sampling.

Remediation Activities

Various remediation efforts along Silver Bow Creek and reaches of the Clark Fork above Deer Lodge began in the late 1980's, with several being completed by 1991 (Montana Superfund Sites Status Report--1994, written commun. USEPA, 1995). Efforts to minimize the input of metals to the Clark Fork from the channel and flood plain below the Warm Springs Ponds involved a combination of in-place stabilization and neutralization of flood plain tailings, plus tailings removal. In addition, dikes have been constructed at the inlet to the Warm Springs Ponds to prevent overflow of Silver Bow Creek flows into the Mill-Willow Bypass.

To reduce the risk of fish kills associated with surface runoff over tailings, berms (low earthen dikes about 30 cm high) were constructed along extensive portions of the Clark Fork streambanks and around floodplain tailings deposits from Warm Springs Creek to Deer Lodge in 1989-90 (Titan Environmental Corporation, 1995,). These berms are designed to retain overland flow from streamside areas and prevent direct discharge of metals-enriched water into the river. In 1990, the Atlantic Richfield Company (ARCO) provided funding to the Montana Governor's Office for a demonstration project using techniques designed to stabilize and/or neutralize tailings in-place. The tailings-affected portions of a 2.4 km reach of the Clark Fork flood plain below Warm Springs Creek was tilled and limed beginning in 1990 and completed in early 1991 (Schafer and Associates, 1996). Vegetation was subsequently planted in these amended soils to provide stability against erosion.

Tailings within the Mill-Willow Bypass have been associated with past fishkills (Clark Fork Superfund Sites, Master Plan, November 1990, written commun. USEPA, 1991). Removal of a large quantity of tailings and contaminated soils (436,000 cubic yards) from a 6 km reach of the Mill-Willow Bypass began in

July 1990 and was completed in early 1991 (Montana Superfund Sites Status Report--1994, written commun. USEPA, 1995).

Dikes at the entry to the Warm Springs Ponds were enlarged during 1992-93 to provide containment of untreated Silver Bow Creek flows of up to 3,300 ft^3/s. Spills from Silver Bow Creek into the Mill-Willow Bypass have not occurred since 1989 (Scott Brown, USEPA, oral commun. 1996). In addition, upgrades of a liming facility used to enhance precipitation and settling of metals was completed in 1992. Other improvements at the Warm Springs Ponds, including inlet and outlet structures and wet- and dry-closure cells, had been completed by 1995 (Montana Superfund Sites Status Report--August 1996, written communication, USEPA, 1996).

On the basis of the chronology of major remediation activities described above, most of the actions undertaken to constrain the predominant sources of metal inputs to the Clark Fork were largely completed between late 1990 and early 1991. Therefore, to aid in evaluating whether possible trends over time in metal transport and bioaccumulation may be related to the timing of remediation activities, the 11-year period of data collection (1985-95) was divided into two intervals for water-quality assessments. The 1985-90 period is considered to generally represent pre-remediation conditions, whereas the 1991-95 period represents the period that could be influenced by remediation activities conducted to date (hereafter termed post-remediation conditions).

SETTING

Basin Characteristics

The Clark Fork above Missoula drains a watershed of 15,400 km^2 in west-central Montana. The Clark Fork Valley, from the confluence of Silver Bow and Warm Springs Creeks to Milltown Dam, is about 150 km long, and ranges in elevation from about 1,460 meters near Galen to about 975 meters near Missoula (fig. 1). The upper Clark Fork primarily lies between two impoundments located at the upper and lower ends of the valley. The Warm Springs Ponds are a series of tailings ponds just upstream of the mouth of Silver Bow Creek. Milltown Reservoir, above Missoula, lies just downstream of the confluence of the Blackfoot River and the Clark Fork. Between these impoundments, numerous small tributaries and several large tributaries contribute flow to the mainstem. The largest tributaries are Warm Springs Creek, the Little Blackfoot River, Flint Creek, Rock Creek, and the Blackfoot River (fig. 1).

River Reach Description

Sampling sites were located along a downstream transect beginning above the Warm Springs Ponds in Silver Bow Creek at Opportunity and ending approximately 280 km downstream at the Clark Fork below Missoula (fig. 1). Sites are identified in river kilometers and miles (table 1), where 0 marks the confluence of Warm Springs Creek and Silver Bow Creek, the beginning of the Clark Fork mainstem. Mainstem sites were located to utilize existing gaging stations and to segment the river such that each intervening reach between mainstem sites brackets either a major tributary or a depositional environment (such as Milltown

Reservoir). Tributaries were also sampled to characterize major hydrologic sources in the upper basin and to provide reference comparisons to the mainstem.

For purposes of discussion, the river will be divided into three reaches. The upstream reach is in the Deer Lodge Valley and includes Silver Bow Creek at Opportunity to the Clark Fork at the confluence of the Little Blackfoot River (-2.1 to 69.7 km). The middle reach encompasses the Clark Fork from the confluence of the Little Blackfoot River to the confluence of Rock Creek (69.7 to 171.4 km. The downstream reach encompasses the Clark Fork from the confluence of Rock Creek to below the Bitterroot River (171.4 to 280 km).

The upstream reach is characterized by extensive floodplain and channel deposits of mine tailings produced by the mining and smelting activities in the Butte-Anaconda area (Brooks and Moore, 1989; Nimick and Moore, 1994). The width of tailings-contaminated land in a 10 km study reach near Galen generally ranged from 189-490 meters, with maximum tailings thicknesses of 30-50 cm mostly occurring in a narrow band near the river (Nimick and Moore, 1994). Tailings 10-30 cm thick are extensive where the floodplain is wide. Thickness declines with distance away from the river. A river survey conducted in 1995 documented that 11.3 percent of the riverbank in the upper reach had visible tailings, with an average bank-tailings thickness of about 14 cm (University of Montana, 1996). These tailings and metal-rich sediments are resuspended by bank cutting and streambed scour as the river meanders through the floodplain, and are transported to downstream reaches. In some areas, thick deposits of tailings on the floodplain have formed unvegetated areas locally termed "slickens", where metal-rich salts form on the surface during warm, dry periods, as metal-rich pore water rises and evaporates (Moore and Luoma, 1990, Nimick and Moore, 1991; Phillips and Lipton, 1995). In the past, dissolution and runoff of these soluble metal salts during summer rainstorms have resulted in fishkills in the upstream reach (Nimick and Moore, 1991; Lambing, 1991; Schafer and Associates, 1996). Stabilization efforts consisting of tailings amendments and berming, appear to have mitigated the lethal effects of summer storm runoff during the post-1990 period of study. However, metal concentrations in bed sediment and biota of the upstream reach are substantially elevated relative to tributaries (table 2). The biological diversity of this reach is low compared to downstream reaches, and the benthic community is characterized by low taxa richness (McGuire, 1988; 1995).

The middle reach of the Clark Fork begins near Garrison and is characterized by a narrowing of the valley floor with lesser amounts of floodplain tailings than in the upstream reach. Approximately 4.9 percent of the visible bank tailings have an average depth of about 7 cm, nearly half of what was measured in the upstream reach (University of Montana, 1996). Moderately elevated metal concentrations have been measured in bed sediment and biota (table 2; see also Axtmann and Luoma, 1991; Cain and others, 1992). Although slicken areas are rare, cutbanks are enriched with metals and metal concentrations in bed sediments are highly variable (Axtmann and Luoma, 1991). The Little Blackfoot River and Flint Creek contribute flow and sediment to the middle reach and generally dilute metal concentrations in the mainstem bed

Table 2: Grand mean (mean of the annual means) metal concentrations in tributaries and mainstem reaches for fine-grained bed sediment (<64um) and aquatic insects (H. cockerelli). Location of tributary input relative to the mainstem is listed in Km (0 Km marks the confluence of Warm Springs Creek and Silver Bow Creek, see Figure 1/Table 1). H. cockerelli was absent from the samples collected in Warm Springs Creek.

		Bed Sediment (<64um), in ug/g dry weight				*H. cockerelli, in ug/g dry weight*			
Tributary	**River Km**	**Cd**	**Cu**	**Pb**	**Zn**	**Cd**	**Cu**	**Pb**	**Zn**
Warm Springs Creek	0	3.9	892	85	421	--	--	--	--
Little Blackfoot River	59.4	0.6	54	43	170	0.6	28	3.6	123
Flint Creek	114.1	2.6	62	189	668	0.4	18.5	7.6	135
Rock Creek	171.4	<1	12	8	48	<0.2	9.7	<1.1	91.6
Blackfoot River*	198.4	<1	21	12	63	0.2	17.6	1.4	145
Mainstem									
Upstream Reach (Galen)	4.7	13	1460	158	2380	1.9	117	7.1	236
Middle Reach (Goldcreek)	85.6	5.9	811	118	1200	1.4	53.3	3.9	168
Lower Reach (Turah)	189.7	3.8	387	80	909	0.9	34.1	4.0	184

*Hydropsyche occidentalis used to compute averages for biota.

sediment in proportion to their inputs (Axtmann and others, 1997). One exception is Pb from Flint Creek which appears to be equally elevated compared to the mainstem and therefore provides no Pb dilution of bed sediments. Taxa richness is higher than in the upstream reach. Species of large caddisfly and stonefly that are absent in the upper reach of the river, first appear below the confluence of the Little Blackfoot, indicating a change in habitat, metal concentration, and/or other environmental conditions (McGuire, 1988; 1995). The upper segment of the middle reach receives the cumulative inputs of metal loads generated from the heavily enriched upstream reach, but inputs from tributaries, such as the Little Blackfoot River and other smaller streams, may improve the habitat and dilute metal concentrations sufficiently to allow for the greater species diversity.

The downstream reach of the river from the Rock Creek confluence to below Missoula is characterized by the least enrichment of metal concentrations in bed sediments and biota (table 2). Metal concentrations in this reach are diluted by inputs from the large drainage areas of Rock Creek, the Blackfoot River, and the Bitterroot River (Axtmann and others, 1997; fig. 1). Nevertheless, concentrations in this lower mainstem reach are still elevated compared to tributaries (table 2; see also Axtmann and Luoma, 1991; Cain and others, 1992). Taxa richness does not appear to be significantly different between Flint Creek and Milltown Reservoir although some aspects of the benthic community change below Rock Creek (McGuire, 1988, 1995). The segment of the downstream reach below Milltown Reservoir is not well studied. The reservoir captures a portion of the metal-rich sediment transported from upstream reaches, although some of the sediment and metal moves through the reservoir (Lambing, 1991). Data for bed sediment and biota in the river segment between Milltown Reservoir and Missoula are insufficient to characterize the effects of metals discharged from the reservoir.

Hydrologic Characteristics

Streamflow varies widely and can be a predominant factor affecting both the quality of water and the amount of suspended sediment and metals transported by water. In general, a wide range of hydrologic conditions occurred during the period of this study (1985-95). Annual streamflow was highest in the Clark Fork in 1986, 1993, and 1995; annual streamflow was lowest during 1988 and 1992 (USGS, issued annually).

Hydrographs of daily mean streamflow at the Clark Fork at Deer Lodge are shown for three different years in figure 2. In general, streamflow in the autumn and early winter periods (October - January) tends to be stable, with little variation in flow magnitude among years. During late winter to early spring, thaws can result in rapid melting of valley snow and breakup of the ice cover that commonly forms during the winter. Runoff during snowmelt can be substantial because frozen soil prevents infiltration of the water. During valley snowmelt, sediments can erode from both the river channel and overland areas, especially where the thawed surface is underlain by frozen soils. The snowpack at higher elevations typically does not melt to any significant degree during such early-season thaws. Consequently, large fluxes of suspended sediment occurring during the late winter and spring snowmelt periods are predominantly from low-elevation sources: channels, floodplains, valley terraces, and foothills. Many of these near-stream sources of sediments are the same areas where extensive deposits of tailings are common. An example of a late-winter snowmelt runoff occurred in February of 1986, resulting in the largest daily flow during 1985-95 (fig. 2). This flow resulted in a large input of suspended sediment into the Clark Fork (Lambing, 1987).

Hydrologic conditions during April and May are transitional between winter and summer. Precipitation can occur as either rain or snow, but the soil is generally thawed and water can infiltrate. The elevation of snowmelt begins to advance up the foothills, and the mountain snowpack begins contributing runoff to the streams. In most years, flow increases during these two months. Sizeable runoff peaks can occur as mid-elevation snowpack melts, and flow is augmented by some high-elevation snowmelt or precipitation runoff. The annual peak flow may occur during this period if temperatures are warm and the snowpack melts early. In contrast, a rare spring drought in 1992 and early irrigation withdrawals resulted in a rapid decrease of streamflow during May (fig. 2). This situation resulted in some of the lowest flows on record for the months of May and June (USGS, issued annually).

Based on long-term streamflow records, the annual maximum daily flow typically occurs during late May to early June in the Clark Fork basin, as a result of both rainfall and melting of the high-elevation snowpack. This condition is illustrated by the hydrograph for water year 1995 (fig. 2). After the peak runoff, streamflow generally decreases gradually during late June. As temperatures increase and precipitation becomes less frequent, declining runoff coupled with irrigation withdrawals typically result in decreasing streamflow during July and August. This decrease may be interrupted temporarily by runoff from summer rain storms. Increasing precipitation and the end of the irrigation season in September results in flow increases.

To help put 1985-95 data into perspective, it is useful to know whether hydrologic conditions during the study period were typical of long-term hydrologic conditions. The best available reference to long-term streamflow characteristics in the upper Clark Fork basin is the record for the Clark Fork above Missoula, which spans water years 1930-95. Streamflow-duration curves, which express the percentage of time that a given streamflow was equaled or exceeded, can be used to compare hydrologic conditions between different periods (fig. 3). Flow-duration curves for the two periods of sediment and metals transport analysis (1985-90 and 1991-95) are very similar. In addition, both curves diverge from the long-term record at the upper streamflow magnitudes, indicating that maximum flows during 1985-95 were less than maximum flows during 1930-95. These differences in flow characteristics probably imply that suspended-sediment discharge, and associated metal loads, have been larger in the past than those measured during 1985-95.

METHODS

Sampling Design

Fourteen sites were sampled for surface water, bed sediment, and biota between Silver Bow Creek at Opportunity and the Clark Fork below Missoula during 1985-95 (table 1). Sites were located throughout the upper Clark Fork basin to provide broad geographic coverage to characterize spatial differences in metal concentrations and to quantify constituent transport along the mainstem as well as from the major tributaries. The network of sites enables an assessment of longitudinal differences between the upper reach of the mainstem, where thick tailings deposits are spatially extensive, to the downstream reach, where tailings are thinner and tributaries modify the water quality. The long-term data provided by the monitoring program enable an assessment of changes in metal concentrations in water, bed sediment, and biota over various types of hydrologic conditions and as remediation progresses.

The surface-water monitoring network was designed to enable quantification of loads from the major tributaries between Warm Springs and Missoula and from the reaches between mainstem sites. Quantification of annual metal loads provides a basin-wide perspective useful for identifying the relative importance of individual source areas, such as tributary basins or channel reaches, and for examining downstream changes in loads. Load estimates for sites bracketing Milltown Reservoir also provide a mass-balance determination of the amount of material deposited in the reservoir and the amount moving through the reservoir to downstream reaches. The density of sampling sites in the network is not sufficient to evaluate the effect of localized metal sources or individual remediation efforts, but is rather designed to provide an assessment of cumulative effects over time using consistent sampling strategies.

The network of bed sediment and biological sampling sites was originally designed to address issues related to specific research topics. Although samples were collected in the basin since 1986, none of the sites was sampled every year during 1986-92. Beginning in 1993, network mainstem sites were sampled every year. Tributary sites are sampled every 1-3 years. Because the different sampling programs were operated independently, several sampling locations for bed sediment and biota were different from water-sampling locations prior to 1992. The location of sampling sites for bed sediment and biota were closely coordinated with the network of 14 surface-water sites since 1992 (table 1). In most instances, the bed sediment and biota sampling sites were re-located to the nearby surface-water sites in 1993. If the new site represented a substantially different environment, the previous data were excluded from long-term trend analysis. The bed sediment and biota data reported for the Clark Fork below Missoula were collected about 57 km downstream from the surface-water site located below Missoula during the entire study period. Bed sediment and biota data were collected 4 km upstream from the surface-water site at Goldcreek prior to 1992, then at the surface-water site since 1992. Similarly; insect data were collected approximately 3 km upstream from the surface-water site at Deer Lodge between 1986 and 1991. From 1992-95 the same site was sampled at Deer Lodge for surface water, bed sediment, and biota.

In order to determine the metal concentration of bed sediment and biota above the Warm Springs Ponds, a site was established on Silver Bow Creek at Opportunity (fig. 1), and was sampled from 1992-95. Tributaries below the Warm Springs Ponds were sampled to establish a reference to temporal trends not associated with remediation (table 1).

Sample Collection

Water-quality and suspended sediment samples were collected at all surface-water sites (U.S. Geological Survey, issued annually). Sampling frequency ranged from 5-10 samples per year at each site. Efforts were made to collect samples over a wide range of hydrologic conditions to document the full range of water-quality variability. The mainstem was sampled more frequently than the tributaries because of the greater variability of hydrologic conditions and inputs from the extensive tailings sources in the Clark Fork channel and floodplain. Tributaries were sampled near their mouths to determine the cumulative contribution from their entire basins. Each site, with the exception of Flint Creek, had a continuous-record streamflow gage that was operated during the entire period of water-quality sampling at the site. A streamflow gage was installed at Flint Creek in 1990.

Cross-sectional water samples were collected from multiple verticals across the stream using depth-integration methods described by Edwards and Glysson (1988), Knapton (1985), and USGS (1977). These sampling methods provide a vertically and horizontally discharge-weighted sample (sample volume proportional to the flow) that is representative of the distribution of dissolved and suspended material in the stream cross section. Sampling equipment consisted of standard USGS depth-integrating samplers (DH-81 and D-74TM) constructed of plastic or equipped with nylon nozzles and coated with a non-metallic paint.

Onsite sample processing, including filtration and sample preservation, was performed according to procedures described by Horowitz and others, (1994), Ward and Harr (1990), USGS (1977), and Knapton (1985). Samples submitted for analysis of dissolved constituents were filtered through a 0.45 μm filter. Instantaneous streamflow at the time of sampling was determined at all sites by direct measurement or from stage-discharge rating tables (Rantz and others, 1982).

Six of the surface-water sites were operated as daily sediment sites (table 1). At those sites, a local observer collected depth-integrated suspended-sediment samples daily during high flow (generally March through June) and 2-3 times weekly during lower flows. The sample concentrations were plotted on a continuous-record hydrograph to construct a continuous sediment-concentration curve. Daily mean suspended-sediment concentration was then determined according to methods described by Porterfield (1972).

Bed sediment and benthic insects were collected simultaneously at the surface water sites during low-flow conditions, typically in August (table 1). Protocols for sample collection and processing are described in detail by Lambing and others, (1995). Bed-sediment was collected from the surface of small deposits in slack waters by the edge of the river, using an acid-washed polypropylene scoop. Three replicate composite samples were collected from several (3-5) such deposits, and samples were collected from both sides of the river wherever possible. These composite samples were then wet-sieved, using ambient river water, through 64μm nylon-mesh sieves. A new nylon-mesh sieve was used at each site. The fine grained (<64μm) fraction was collected in acid-washed 500 mL polyethylene bottles and transported to the laboratory on ice.

Individual samples of bulk bed sediment (<10 mm) also were collected from the surfaces of 3-5 randomly selected deposits. The unsieved samples were composited and stored in acid-washed polyethylene bottles that were transported to the laboratory on ice (Dodge and others, 1996).

Benthic insects were collected from a single riffle at each site. Samples were obtained by repeated collections employing a nylon-mesh kick net until an adequate number of individuals was collected to provide sufficient mass for analysis (~250 mg dry weight per sample). Taxa targeted for collection included two caddisflies, *Hydropsyche spp.* and *Arctopsyche grandis* (Trichoptera), and the stonefly *Claassenia sabulosa* (Plecoptera). *Hydropsyche spp.* and *A. grandis* are net-spinning, omnivorous, filter feeders, and *C. sabulosa* is a predator (Merritt and Cummins, 1984). Each taxon was sorted to genus and stored separately in acid-washed plastic containers filled with ambient river water. Containers were kept on ice to allow the insects to evacuate their gut contents for a period of six to eight hours. Excess water was drained and insects were frozen for transport to the laboratory.

Sample Preparation and Analysis

Periodic cross-sectional water samples were analyzed for dissolved and total-recoverable concentrations of arsenic (As), cadmium (Cd), copper, (Cu), iron (Fe), lead (Pb), manganese (Mn) and zinc (Zn) by the USGS National Water Quality Laboratory. Analytical methods are described by Fishman (1993). Samples were also analyzed for suspended-sediment concentration and particle size distribution (percent finer than 0.062 mm in diameter), according to methods described by Guy (1969) and Lambing and Dodge (1993).

Bed sediment samples were dried in an oven at 60°C, and ground to a homogenous consistency using an acid-washed ceramic mortar and pestle. Replicate aliquots of approximately 0.6 grams of sediment were digested using a hot, concentrated (16 M) nitric acid (HNO_3) reflux digest (Luoma and Bryan, 1981). After a digestion period of up to several weeks, samples were evaporated to dryness, and redissolved with 20 mL of 0.6N hydrochloric acid (HCl). The reconstituted samples were filtered through a 0.45μm filter with a syringe and in-line disposable filter. The filtrate was diluted 1:5 or 1:10 with 0.6 N HCl, and analyzed for Cd, Cr, Cu, Fe, Mn, Ni and Zn, using Inductively Coupled Argon Plasma Emission Spectroscopy (ICAPES). Silver and Pb were analyzed by Atomic Absorption Spectroscopy (AAS).

Insects were thawed and rinsed with ultra-pure deionized water to remove any surface particulate material. *H. cockerelli* was separated from other species of hydropsychid caddisflies (Schefter and Wiggins, 1986). Approximately 50-100 individuals were composited into replicate samples where possible (in nearly all collections from 1992-1995). When large numbers of individuals were collected from a site, each composite was restricted to similar-sized individuals. Insect samples were placed in a tared scintillation vial and dried at 70°C. Samples were weighed to obtain a final dry weight and digested by reflux using concentrated HNO_3 (Cain and others, 1992). After digestion, samples were evaporated to dryness. The residue was reconstituted in 0.6 N HCl, filtered through a 0.45μm filter, and analyzed for Cd, Cr, Cu, Fe, Mn, Pb, and Zn by ICAPES.

Quality Assurance

Quality-assurance (QA) procedures used for the collection and field processing of water-quality samples are described by Horowitz and others (1994), Ward and Harr (1990), Edwards and Glysson (1988), Knapton and Nimick (1991), and Knapton (1985). Standard procedures used by the USGS National Water Quality Laboratory for internal sample handling and quality assurance are described by Friedman and Erdmann (1982), Jones (1987), and Pritt and Raese (1995). Quality-assurance procedures used by the Montana District sediment laboratory are described by Lambing and Dodge (1993).

Analytical results for water were evaluated using quality-control (QC) samples that were submitted from the field and analyzed concurrently in the laboratory with routine environmental samples. Samples consisted of replicates, spikes, and blanks and provided quantitative information on the precision and bias of the overall field and laboratory process. Each type of QC sample was submitted at a proportion equivalent to about 5 percent of the total number of samples, with all QC samples collectively constituting about 15 percent of the total number of samples submitted for analysis.

QC samples for bed sediment and biota consisted of procedural blanks and standard reference material (SRM). Analytical results for blanks and percent recoveries of the SRM's are reported in Lambing and others, (1994; 1995; Dodge and others, 1996). Each type of QC sample was analyzed in a proportion equivalent to about 10-20 percent of the total number of samples.

SPATIAL AND TEMPORAL TRENDS OF TRACE METALS

Surface Water

Analyses of samples collected from streams during 1985-95 were used to characterize water quality and the fluvial transport of suspended sediment and metals. Constituent concentrations, correlations among related hydrologic variables, and streamflow data were used to calculate annual sediment and metals transport rates at each of the network sites. This information was then used to identify the relative contributions from various source areas and evaluate possible trends in transport rates.

Transport Characteristics of Suspended Sediment and Metals. Suspended sediment and metals transported through the upper Clark Fork basin during 1985-95 were affected by both the hydrologic conditions and availability of sediment and metals throughout the basin. The delivery of either dissolved or particulate forms of metal from source areas to streams affects not only the water-borne chemical exposure to biota, but also the metal content of bed sediment. Suspended sediment and precipitates of dissolved metals can settle to the streambed and reside for extended periods of time. The metal can be redistributed within the river, especially during periods of high flow when resuspension and transport is at a maximum. Subsequent redeposition can result in accumulation patterns within the bed sediment that vary with location and over time. Because the streambed is the physical habitat of many aquatic insect larvae, variable levels of metal deposition may influence the exposure risk to the biota that live within or in close association with bed sediments.

Computational methods used to estimate annual loads of suspended sediment and metals are described in Appendix A. Analysis of total-recoverable metals transport for 1991-95 was limited to Cu, Pb, and Zn. Equations used to estimate suspended-sediment and total- recoverable metals transport for water years 1991-95 are presented in Appendix A, tables 1-4. Regression equations for sediment and total-recoverable metals transport for water years 1985-90 are presented in Lambing (1991). Adjustment of 1985-90 loads for potential bias associated with previous analytical methods is described in Appendix A.

Seasonal differences in sediment-transport characteristics were observed at most sites (fig. 4). Separate equations were employed to describe sediment transport at these sites for each of two seasons: January-May and June-December. A similar segregation of data by season also was used to calculate suspended-sediment loads for 1985-1990 (Lambing, 1991). The two seasons were segregated on the basis of differences in sediment-discharge between late-winter/early-spring valley snowmelt and late-spring/summer mountain snowmelt. Typically, suspended-sediment concentrations were higher during the valley-snowmelt period compared to the mountain-snowmelt period. For sites not displaying a strong seasonal difference in sediment discharge, a single equation was used.

Because most of the Cu, Pb, and Zn loads in the Clark Fork are associated with sediment particles (Lambing, 1991), transport rates of metals closely reflect rates for suspended sediment. A strong relationship between total-recoverable Cu discharge and suspended-sediment discharge (fig. 5) indicates that suspended-sediment discharge explains much of the variability in metal-transport rates. Consequently, determination of the seasonal variability in suspended sediment is important for estimating annual loads of total-recoverable metals.

Analysis of dissolved metal transport was limited to Cu because dissolved Pb and Zn commonly occur at concentrations below analytical detection limits which precludes development of statistical correlations. Regression equations describing dissolved Cu transport for water years 1985-90 and 1991-95 are presented in Appendix A, tables 5 and 6, respectively. Data used to develop equations for dissolved Cu discharge for 1985-90 have been adjusted for analytical bias as described in Appendix A.

A summary of estimated average annual loads of suspended sediment and total-recoverable Cu, Pb, and Zn for 1991-1995 are shown in Appendix A, tables 7-10. Tables of average annual loads for water years 1985-90 are presented in Lambing (1991). Estimated average annual dissolved Cu loads for both time periods are shown in Appendix A, tables 11 and 12.

Annual loads were estimated for mainstem and tributary sites using the transport equations and daily records of either streamflow or suspended-sediment load. Loads were also estimated for intervening reaches between mainstem sites as the difference in mainstem loads, minus the load from gaged tributaries entering the reach. Metal inputs along intervening reaches are assumed to be derived from ungaged tributaries, ground-water discharge, or the mainstem channel and flood plain. The proportion of intervening load from each of the potential sources is undetermined.

Spatial Patterns. The average annual load of metal passing each site in the network can be presented as a percentage of the total load discharged to Milltown Reservoir. Percentages of the total load during 1991-95 are presented in table 3; load percentages for 1985-90 are presented in Lambing (1991). The proportion of local contributed to Milltown Reservoir indicates the relative importance of tributaries and different reaches of the mainstem as source areas supplying sediment and metals to the Clark Fork.

The Clark Fork contributed a substantially larger proportion of Cu, Pb, and Zn to Milltown Reservoir than the Blackfoot River during both 1985-90 and 1991- 95. During 1991-95, an estimated 84 percent of the Cu, 70 percent of the Pb, and 81 percent of the Zn discharged to Milltown Reservoir originated from the Clark Fork basin above Turah Bridge, although the Clark Fork contributed only 48 percent of the total suspended-sediment load to the reservoir. Thus, in both 1985-90 and 1991-95, sediment from the Clark Fork was enriched in metal relative to that of the Blackfoot River. There was little difference between the two time periods in the proportion of total loads and streamflow discharged to Milltown Reservoir by the two rivers.

The four major tributaries between Warm Springs Ponds and Turah Bridge (Warm Springs Creek, Little Blackfoot River, Flint Creek, and Rock Creek) contributed only a minor proportion of the total metal discharged to Milltown Reservoir (table 3). For example, only 3 percent or less of the Cu discharged during 1991-95 came from any individual tributary above

Table 3. Percentage of average annual suspended-sediment and total-recoverable metal loads discharged to Milltown Reservoir from various source areas and the cumulative proportion of the load passing mainstem sites during 1991-95

Location	Suspended Sediment		Copper		Lead		Zinc	
	Source	*Cumulative Sum*	Source	*Cumulative Sum*	Source	*Cumulative Sum*	Source	*Cumulative Sum*
Silver Bow Creek at Warm Springs	1.2		8		1.7		10	
Warm Springs Creek at Warm Springs	0.9		2.3		1.7		1.1	
Intervening reach (6.8 Km)	0.8		4.6		1.7		2.1	
Clark Fork near Galen		*2.9*		*15*		*5.1*		*13*
Intervening reach (39.9 Km)	7.9		30		17		17	
Clark Fork at Deer Lodge		*11*		*45*		*22*		*31*
Little Blackfoot River near Garrison	4.9		1.1		3.4		2.1	
Intervening reach (41 Km)	6.3		6.5		6.8		9.9	
Clark Fork at Goldcreek		*22*		*53*		*32*		*43*
Flint Creek near Drummond	4.2		1.5		12		5.6	
Intervening reach (50.4 Km)	10		14		12		19	
Clark Fork near Drummond		*36*		*68*		*56*		*68*
Rock Creek near Clinton	6.7		2.7		5.1		4.7	
Intervening reach (53.7 Km)	5		13		8.5		8.4	
Clark Fork at Turah Bridge		*48*		*84*		*70*		*81*
Blackfoot River near Bonner	52		16		30		19	

Turah Bridge. One exception was Flint Creek, which contributed 12 percent of the Pb load to Milltown Reservoir. The proportional contribution of metal load from the tributaries during 1991-95 was similar to that during 1985-90.

A large proportion of the metal input to Milltown Reservoir came from sources in the intervening reaches. For example, the 6.8 km reach between Silver Bow Creek at Warm Springs and Clark Fork near Galen contributed approximately twice the Cu and Zn load of the entire Warm Springs Creek basin during 1991-95 (table 3). The largest single contribution to the metal load entering Milltown Reservoir from the Clark Fork above Turah Bridge came from sources within the 39.9 km reach between Galen and Deer Lodge (30 percent of Cu, 17 percent of Pb, and 17 percent of Zn during 1991-1995). The reach between Deer Lodge and Goldcreek contributed only 6.5 percent of the total Cu input to Milltown Reservoir during 1991-1995, whereas the next two reaches (Goldcreek to near Drummond and near Drummond to Turah Bridge) each contributed about 13-14 percent to Milltown Reservoir (table 3).

Because the lengths of intervening reaches vary, load inputs expressed on a unit-length basis (tons per river km) can be useful in comparing the intensity of metal input among reaches. If the assumption is made that most of the total-recoverable metal input comes from the channel and flood plain, then dividing the total load

Table 4. Estimated average annual suspended-sediment and total-recoverable metal loads per river kilometer potentially contributed from channel and flood-plain sources in the intervening reaches of the upper Clark Fork during water years 1991-95. Loads per unit-length of river are based on an assumption that other unmeasured sources (ground water, ungaged tributary inflow) within each reach are negligible.

Intervening reach between mainstem staions	Average annual load, in tons per river km			
	Suspended Sediment	*Copper*	*Lead*	*Zinc*
Silver Bow Creek at Warm Springs to Clark Fork near Galen (6.8 Km)	79.9	0.18	0.02	0.15
Clark Fork near Galen to to Clark Fork at Deer Lodge (39.9 Km)	136	0.20	0.03	0.20
Clark Fork at Deer Lodge to Clark Fork at Goldcreek (41.0 Km)	106	0.04	0.01	0.11
Clark Fork at Goldcreek to Clark Fork near Drummond (50.4 Km)	137	0.07	0.01	0.18
Clark Fork near Drummond to Clark Fork at Turah Bridge (53.7 Km)	64.2	0.07	0.01	0.07

contributed from the intervening reach by the total reach length can provide an estimate of linear yield of metal. Although metal is presumably not contributed in uniform quantities along the entire length of a reach, such a measure serves as an approximation of average linear yield. Knowledge of reaches with high unit-length inputs of metal can provide insight into the potential for localized effects on water quality or metal accumulation in the bed and biota. In addition, determination of spatial differences in metal yields can be useful for evaluating remediation options.

The greatest Cu and, to a lesser degree, Pb and Zn, inputs per river km occurred in the two intervening reaches above Deer Lodge (table 4). Total-recoverable Cu inputs per river km above Deer Lodge were 3-5 times greater than in any of the downstream intervening reaches, although suspended-sediment inputs were generally similar. This load gradient is likely a function of a decreasing metal-concentration gradient in the channel and flood-plain sediment with distance from the headwater mining area (Axtmann and Luoma, 1991). Based on the assumption that the channel and flood plain are the primary metal sources in intervening reaches, it appears that Cu inputs from erosional processes associated with meander migration across the flood plain are greatest in the reach between the Warm Springs Ponds and Deer Lodge.

The spatial patterns of dissolved Cu loads during water years 1991-95 (Appendix A, table 12) offer insight into the relative importance of various source areas for the soluble phase of Cu. However, the statistical correlations used to estimate dissolved Cu loads are not as strong as those for total-recoverable Cu; therefore, the spatial patterns are considered to be more general. Copper was the only metal for which transport rates of the dissolved phase were evaluated. Table 5 lists the percent of the dissolved Cu load entering Milltown Reservoir that was contributed from various source areas, and the unit-length yield for each intervening reach.

Similar to total-recoverable Cu loads, sources within the intervening reaches between mainstem sites accounted for a substantial proportion of the dissolved Cu discharged to Milltown Reservoir during 1991-95. Tributaries above the Clark Fork at Turah Bridge generally contributed about 5 percent or less to the reservoir. Overall, the Clark Fork contributed 75 percent of the dissolved Cu, whereas the Blackfoot River contributed only 25 percent.

A notable difference in the unit-length contribution of dissolved Cu compared to total-recoverable Cu is the lack of a substantial difference between the upstream and downstream intervening reaches during 1991-95. The reaches between Deer Lodge and Goldcreek, and between Drummond and Turah Bridge yielded similar amounts of dissolved Cu per river km as the reach between Galen and Deer Lodge. Two reaches appeared to contribute very little dissolved Cu per river km — between Silver Bow Creek at Warm Springs and the Clark Fork near Galen, and between Goldcreek and near Drummond. It is uncertain whether the lack of a detectable dissolved Cu load in the reach between Silver Bow Creek at Warm Springs and the Clark Fork near Galen was due to a negligible amount of source material, an inadequately defined dissolved Cu transport relation, or a reach length too short to allow spatial resolution of small loads. The unit-length load between Gold Creek and near Drummond is 4-5 times smaller than the other reaches of similar length. The reason for this decrease in dissolved Cu yield in a reach bounded by higher yields is unknown.

<u>Temporal Patterns</u>. The current network of sampling sites was designed to track long-term patterns of metal transport and accumulation among multiple environmental indicators at key locations in the basin. Because 1985-95 spans both pre- and post-remediation periods, the data may be useful in identifying changes coincident with the major remediation activities undertaken from the Warm Spring Ponds to Galen. Effects from specific remediation efforts or other land-use activities will be difficult to determine from the data, however, because of the widespread metal sources in the basin, the wide range of annual hydrologic conditions during 1985-95, and the relatively large distance between monitoring sites.

Large variations in annual loads do not necessarily imply that a change has occurred in the supply of a constituent; annual loads can vary simply as a function of the amount of runoff available to transport materials. As a preliminary assessment, graphical analysis is used to identify concurrent patterns of annual

Table 5. Percentage and yield of dissolved copper load per river kilometer discharged to Milltown Reservoir from various source areas, water years 1991-95.

Location	% Average Annual Cu Load to Milltown Reservoir *Source*	*Cumulative Sum*	Estimated Average Annual Dissolved Cu Yield (tons per river Km)*
Silver Bow Creek at Warm Springs	18		
Warm Springs Creek at Warm Springs	2.5		
Intervening reach (6.8 Km)	0.0		0.000
Clark Fork near Galen		20	
Intervening reach (39.9 Km)	13		.020
Clark Fork at Deer Lodge		33	
Little Blackfoot River near Garrison	2.5		
Intervening reach (41.0 Km)	12		.018
Clark Fork at Goldcreek		47	
Flint Creek near Drummond	2.6		
Intervening reach (50.4 Km)	3.0		.004
Clark Fork near Drummond		53	
Rock Creek near Clinton	5.1		
Intervening reach (53.7 Km)	17		.019
Clark Fork at Turah Bridge, near Bonner		75	
Blackfoot River near Bonner	25		

*Unit-length dissolved Cu yield assumes that inputs from ungaged tributaries are negligible.

transport for related hydrologic variables. Divergent patterns among variables that typically have similar transport characteristics could be indicative of a disproportionate change in the supply or delivery of one of the constituents. Ultimately, rigorous statistical analyses of sample concentrations measured over time, correlations among variables, adjustments for streamflow effects, and equivalency of analytical results as changes in methodology are implemented would be necessary to detect significant incremental trends that represent a real change in the aquatic environment.

A plot of annual suspended-sediment discharge and streamflow during water years 1985-95 for the Clark Fork at Deer Lodge (fig. 6) indicates the effect of runoff variability on the transport of sediment. Although annual sediment discharge fluctuates in a manner generally similar to annual flow volumes, it is evident by the lack of parallel hydrographs that other factors may act to increase or decrease sediment inputs and, by association, metal inputs.

To evaluate the possible effect of hydraulic energy on sediment transport, annual suspended-sediment discharge at Deer Lodge was plotted against the maximum daily streamflow for each year (fig. 7). This plot shows a nearly parallel pattern for maximum streamflow and sediment discharge, which illustrates that the magnitude of annual peak flows have a strong influence on the annual load of sediment. Because the parallel pattern of maximum daily flow and annual sediment discharge did not diverge during 1985-95, there likely was no significant change in sediment delivery to the Clark Fork in the basin above Deer Lodge during the period. The substantial effect of peak flow energy on the movement of constituents through the basin emphasizes the importance of obtaining samples during high flows to adequately define transport characteristics.

Concurrent transport patterns for related variables such as total-recoverable Cu and suspended sediment may help to detect changes associated with factors other than annual runoff variability. Diverging patterns that persist over time might indicate a sustained change in constituent supply or delivery. Hypothetically, if the fundamental conditions of metal availability and transport are unchanged, the two time-series plots would be expected to be parallel. Conversely, if either the supply or delivery process changes, then the two curves might diverge from a parallel pattern, thus indicating a change in the amount of Cu transported relative to sediment. To support the existence of an apparent trend, however, would probably require that the diverging pattern be sustained for a series of consecutive years and over a wide range of hydrologic conditions.

Annual loads of suspended sediment and total-recoverable Cu for the 1985-95 period at the Clark Fork near Galen (fig. 8) followed similar annual fluctuations of increase and decrease, but a downward shift of Cu discharge relative to sediment discharge is evident beginning in 1991. The pattern of Cu load relative to suspended-sediment load was variable for the other two long-term mainstem sites at Deer Lodge and at Turah Bridge. Notably, there was no decrease at Deer Lodge (fig. 9), and possibly a small increase in Cu load relative to sediment load in the 1990's compared to the high sediment-discharge years of 1986 and 1989. The different patterns observed at Galen and Deer Lodge indicate that the mechanisms that caused the downward shift in Cu transport at Galen were insufficient to cause detectable changes at Deer Lodge. At Turah Bridge, the data indicate a post-1990 decline in Cu load relative to sediment load (fig. 10) similar to that observed at Galen. At the Clark Fork above Missoula (below Milltown Reservoir), there was no apparent change over time (Appendix A, fig. 3).

Temporal patterns of metal transport in the mainstem were compared to patterns in tributaries that have not undergone remediation activities. For example, an apparent downward shift in the magnitude of annual Cu load relative to suspended-sediment load in Flint Creek (fig. 11) is similar to that for the Clark Fork near Galen. Other tributaries (Appendix A, figs. 4-6) show variable patterns over time, ranging from a downward shift in Cu transport at the Little Blackfoot River to an upward shift at Rock Creek. Temporal patterns in relative rates of transport in tributaries, however, are difficult to assess because the low Cu concentrations make the annual load estimates very sensitive to the 1985-90 bias adjustments (see Appendix A). The lack of distinctly different patterns of Cu transport between mainstem and some tributary sites complicates the interpretation of possible remediation-induced trends in the mainstem, and may indicate that additional hydrologic factors are affecting transport.

Temporal patterns of total-recoverable Pb and Zn loads during 1985-95 were somewhat different than those for Cu. Patterns of Pb transport do not appear to vary over time relative to sediment transport in the unremediated tributaries, with the exception of the Blackfoot River which showed a slight downward shift. This pattern may be partly a computational artifact because the correlation between total-recoverable Pb discharge and sediment discharge for the 1985-90 period was not very strong (Lambing, 1991). More notably, there is no decrease in Pb transport indicated at Galen as there was for Cu. If the decreased Cu loading was indicative of remediation-induced loading reductions, then total-recoverable Pb sources in the basin upstream of Galen have not been similarly decreased by remediation. At Deer Lodge, Pb transport relative to sediment also shows no decrease during 1985-95. The Clark Fork at Turah Bridge shows a downward shift in Pb transport; but because the upper mainstem sites showed no apparent remediation effect on total-recoverable Pb transport, this may be further evidence of a potential basin-wide hydrologic effect. However, the apparent trends for Pb may be inconclusive because of the sensitivity of the low concentrations to bias adjustment. Zinc loads do not show a clear trend at any of the sites.

Dissolved Cu transport was also examined relative to annual streamflow to evaluate possible temporal trends. The estimation of dissolved Cu loads is described in Appendix A. In general, dissolved Cu discharge closely paralleled annual streamflow at most sites (Appendix A, figs. 7-13). The Clark Fork near Galen and at Deer Lodge are possible exceptions, as indicated by the divergence of the curves. The time-series plot for Deer Lodge (fig. 12) illustrates the diverging pattern observed at both of the upper mainstem sites, whereby a downward shift occurred during 1993-95. The short duration of the shift may be inconclusive in terms of a sustained trend, but it is notable that these two mainstem sites are nearest the remediated areas of surface slickens -- a source of soluble Cu salts.

Hydrologic Effect On Trends. Long-term trends in Cu transport that represent actual changes in Cu supply or delivery can be difficult to distinguish from natural variability in Cu loads caused by annual differences in runoff. Because Cu is strongly associated with sediment, a single measure of transport that incorporates Cu and sediment load simultaneously might be a useful indicator with which to evaluate temporal changes in the Cu content of suspended sediment. Such a measure can be represented by the ratio of annual total-recoverable Cu load to annual suspended-sediment load. Annual mass ratios may help to discern trends that might otherwise be obscured by the large amount of variability in annual loads.

The Cu:sediment mass ratios during 1985-95 can be plotted as an annual time series and fit with a LOWESS-smooth line (Cleveland, 1979) to determine the overall direction of any temporal pattern, or whether directional changes in slope occurred during the period. Directional changes in slope can be examined relative to streamflow magnitude or for coincidence with the timing of remediation activities to infer possible effects on total-recoverable Cu transport. There is no statistical test of significance associated with the smoothing calculation, but a weighting procedure minimizes the effect of individual extreme values to provide a general indication of the predominant direction over time.

The LOWESS-smooth line for the Clark Fork near Galen (fig. 13) indicates a downward shift in slope for the Cu:sediment ratios after 1988 and continuing through 1995. The sustained downward slope for seven consecutive years possibly infers a decrease in Cu supply or delivery relative to that of sediment, but the start of the downward shift precedes the period of major remediation activities. The LOWESS-smooth line for the Clark Fork at Deer Lodge (fig. 14) shows a distinctly different temporal pattern than that for the Clark Fork near Galen. The apparent trend is slightly upward through 1992, with a downward shift in slope after 1992. This pattern may indicate either no significant change, or possibly even a slight increase in Cu delivery relative to sediment delivery. These observations are qualitative, however, and should be viewed with caution, especially given the relatively wide range of ratios.

Temporal patterns in tributaries can be similarly evaluated to indicate annual differences in Cu:sediment ratios. The LOWESS-smooth line for Flint Creek (fig. 15) indicates a downward slope since 1988, similar to that observed for the Clark Fork near Galen. As with the mainstem near Galen, this temporal pattern also infers a decrease in Cu transport relative to sediment transport, but in a basin that has not undergone large-scale remediation. The lack of a physical basis, such as remediation, to explain an apparent decrease in Cu transport could indicate that other factors unrelated to remediation are contributing to a difference in the relative quantities of Cu and sediment delivered to the streams.

Although the Cu:sediment mass ratios provide a single integrated measure of the annual variability in transport, it is not known whether the annual variability of streamflow can affect the ratios and cause apparent temporal trends, even when the Cu supply or delivery processes are unchanged. To test this hypothesis, the annual Cu:sediment ratios were plotted against annual streamflow to see if mainstem and tributary sites display a common relationship that might indicate a basin-wide hydrologic effect on trends. In the absence of a relationship with streamflow, sustained temporal patterns may be more likely to represent an actual trend caused by changes in Cu supply or delivery.

A plot of annual Cu:sediment ratios against annual streamflow for the Clark Fork near Galen for 1985-95 (fig. 16) indicates a statistically significant inverse relation (R^2 = .74, $p = <.001$). As annual streamflow increases, the Cu:sediment ratios decrease. Four of the five lowest ratios occurred during the post-remediation period of 1991-95 (1991, 1993-95). Three of these years had the highest flows since 1986. Because ratios decrease with increasing flow, the recent downward slope of the LOWESS-smooth line for Galen (fig. 13) may simply be the result of increased runoff in recent years. In addition, the Cu:sediment ratio for the year of highest flow (1986) during the pre-remediation period shows essentially no difference from ratios for similar flows (1993-94) in the post-remediation period, further indicating that input processes for total-recoverable Cu have not changed substantially above the Clark Fork near Galen.

At the Clark Fork at Deer Lodge, there is no statistically significant relationship between annual Cu:sediment ratios and annual streamflow (R^2=.21, p=.15), although there appears to be a weak inverse relation (fig. 17). This lack of a significant relation is also supported by the LOWESS-smooth trend which is slightly upward (Fig. 14). Thus, there is no evidence that the Cu content of suspended sediment is decreasing at Deer Lodge as a result of either hydrologic effects or anthropogenic activities in the basin upstream.

The Blackfoot River shows a statistically significant inverse relation (R^2 = .56, p=.01) between Cu:sediment ratios and annual streamflow (fig. 18) similar to that for mainstem sites. This is notable, because the highest annual flows occurred in different years than in the Clark Fork, yet the relation of decreasing ratios with increasing flow still held. Consequently, decreases in Cu:sediment ratios with increasing flow are not unique to the mainstem or any particular period of time.

The inverse relation of Cu:sediment ratio to annual streamflow magnitude was exhibited to varying degrees at all the sampling sites, indicating at least some effect on Cu transport trends by annual hydrology. A possible explanation for this apparent hydrologic effect in the mainstem could be that, at least at some sites, during years of high precipitation and streamflow, a proportionately greater amount of sediment low in Cu content is contributed by tributaries and/or overland runoff, resulting in Cu dilution and lower annual Cu:sediment ratios. In years of low precipitation and runoff, channel sediments having a relatively higher Cu content presumably would be less diluted by other sediment inputs, resulting in a higher ratio.

The same process of Cu dilution by sediments originating outside of channel sources may also occur to varying degrees in the tributaries. Given the fact that small- to moderate-scale mining has occurred in many tributary basins, it is likely that at least limited amounts of tailings have been introduced and dispersed along tributary channels or flood plains. If this is the case, then the dilution effect from sediment sources outside of tributary channels might be discernible and lead to relations of Cu:sediment ratios to streamflow that are similar to that of the mainstem.

Although the hydrologic effect on Cu:sediment ratios does not necessarily imply that a remediation effect is absent, it does complicate efforts to detect remediation-induced trends. Regardless of the specific mechanism controlling Cu:sediment ratios, it appears that the level of Cu in suspended sediment is dependent on the proportion of sediment derived from channel and non-channel sources. Because these proportions probably vary with annual flow volumes, understanding remediation-induced trends in Cu transport may require first understanding natural hydrologic trends.

Statistical Comparison of Copper Relations. Temporal patterns in annual loads relative to annual streamflow indicate the long-term variability of metals transport throughout the basin under different hydrologic conditions. The determination of annual loads, however, requires extensive analysis of correlation between variables followed by subsequent calculations using daily streamflow records. Therefore, the accuracy of calculated loads is dependent on the level of potential error associated with each of the numerous estimation procedures. To minimize the effect of computational error in analysis of incremental annual trends, sample concentrations, rather than computed loads, were used directly to assess possible changes in metal concentrations between two time periods.

Regression relations that describe the response of Cu concentrations to related hydrologic variables were developed for the 1985-90 (pre-remediation) and 1991-95 (post-remediation) periods. These relations were statistically tested for significant differences between the two periods. If the regression equations for each period are different, it may imply that a process has changed that controls either the supply or rate of delivery of Cu to the river. The lack of a statistical difference in relations for two time periods may imply no change in Cu input processes, regardless of the annual variations in loads. Although this type of analysis cannot provide a measure of incremental trend over time, it does give insight into potential process changes between two periods of time. Because this time separation coincides with pre- and post-remediation activities, differences in relations may infer an effect from remediation.

Analysis of covariance was used to test for significant difference in intercept and slope between regression relations developed for the two periods at seven long-term sites. Regression relations of log-transformed data were tested for both total-recoverable and dissolved Cu concentrations. All Cu data for 1985-90 were adjusted for analytical bias before testing, as described in Appendix A. Because of bias adjustments and unequal sample sizes, equations were considered statistically different at a significance level of $p<0.10$. Regression relations were tested by the two-tailed ANCOVA procedure (Statware, Inc., 1992).

Results of covariance testing indicated that there was no significant difference in the relation between total-recoverable Cu concentration and suspended-sediment concentration between 1985-90 and 1991-95 at any of the mainstem sites above Milltown Reservoir. In effect, for a given suspended-sediment concentration, the same total-recoverable Cu concentrations were present after remediation as before. The similarity of relations between the two time periods is illustrated in the regression plots for the Clark Fork at Deer Lodge (fig. 19).

There also was no difference in total-recoverable Cu relations between the two time periods for Flint Creek and Rock Creek. Statistically significant differences were noted in the relations for the Little Blackfoot River ($p = 0.10$) and the Blackfoot River ($p=0.03$). In both cases, the 1991-95 intercepts were lower, indicating generally lower total-recoverable Cu concentrations for a given suspended-sediment concentration. It is unknown what the physical basis is for a decreased Cu supply or delivery rate in these two tributaries. It is possible that streams with typically low Cu concentrations are overly sensitive to the 2 ug/L bias adjustment made to the 1985-90 data. Also, because the strength of correlations for low-Cu streams are generally weak, any statistical comparison of change in the relations is subject to considerable uncertainty.

Relations for dissolved Cu concentration also tended to be weak because of the generally low values and narrow range of concentrations at most sites. Results of covariance testing for regression relations between dissolved Cu concentration and streamflow for 1985-90 and 1991-95 revealed somewhat different results than those for total-recoverable Cu. None of the tributaries showed any significant difference in relations between the two time periods. However, two mainstem sites, the Clark Fork near Galen and at Deer Lodge (fig. 20), indicated weak, but statistically significant differences for the pre- and post-remediation periods ($p = 0.07$ for both sites). The 1991-95 intercepts were lower at both sites, indicating lower dissolved Cu concentrations for a given streamflow in the post-remediation period. No difference between the two time periods was evident at Turah Bridge.

Covariance tests on weak correlations between dissolved Cu and streamflow (R^2 values typically 0.2-0.3) are limited in the strength of conclusions that can be drawn. In addition, the 1 ug/L bias adjustment applied to the 1985-90 dissolved Cu concentrations, possibly could affect the test for differences between the two time periods. However, the downward shifts in dissolved Cu relations indicated for the Clark Fork near Galen and at Deer Lodge might be expected from the remediation of exposed flood plain tailings near these sites. The Cu sulfate salts that commonly form on the surface of the slicken deposits are soluble and have been shown to contribute large loads of dissolved Cu during overland runoff (Schaffer and Associates, 1996). The decreased potential for inputs of dissolved Cu from treated slickens may explain a concurrent decrease in dissolved Cu concentrations in adjacent reaches of the Clark Fork. The decreases, if real, are presumably too small to be statistically discernible further downstream at the Clark Fork at Turah Bridge.

In contrast to dissolved Cu, the lack of a statistically significant difference for total-recoverable Cu concentrations at the Clark Fork near Galen and at Deer Lodge might also have a physical basis consistent with site conditions. If it is assumed that the stream bank and bed sediments are the primary sources of particulate (suspended) Cu, then erosion of these channel materials would need to be decreased in order to cause a detectable decrease in total-recoverable concentrations, of which about 80 percent consists of suspended Cu (Lambing, 1991). The remediation efforts completed through 1995 have focused on exposed surface tailings and runoff rather than channel-erosion processes (bank cutting and bed scour); therefore, if metal availability from channel sources has not changed over time, particulate Cu inputs may be responding to erosion rates controlled by annual hydrologic conditions. The complex responses of metal transport to the combined effects of natural variability and remediation point to the need to evaluate other indicators of metal pathways and exposures.

Bed Sediment

Both fine-grained bed sediments (<64 μm) and bulk bed sediments (<10mm) were analyzed in this study, but unless stated otherwise, interpretations are confined to the fine-grained bed sediment data. Particle size in the substrate varies from cobbles to clays in the Clark Fork, and the particle-size distribution of a sediment sample can greatly influence metal concentrations (Salomons and Forstner, 1984). Sieving bed sediment samples to a common size class of particles allows comparisons of metal concentrations to be standardized among sites and reduces potential biases that could distort interpretations of the spatial distribution and trends in metal concentration. Fine particles are also trapped within the matrix of periphyton and filamentous algae that are part of the microhabitat of many insect species. Fine-grained sediment along a concentration gradient have correlated significantly to metal concentrations in benthic insects and are a useful indicator of the metal exposure to the biota (Cain and others, 1992, Kiffney and Clements, 1993; Cain and others, 1995).

Tributaries. Samples of fine-grained bed sediment were collected from tributaries as a reference to concentrations and temporal trends in the mainstem (table 2). Rock Creek and the Blackfoot River had the lowest concentrations of metals and are used as the primary reference to determine relative enrichment of metals in the mainstem. Warm Springs Creek (which drains the Anaconda smelting complex), the Little Blackfoot River, and Flint Creek had mean concentrations of Cd, Cu, Pb and Zn that were elevated compared to Rock Creek and the Blackfoot River.

Metal concentrations in the bed sediments of most tributaries were low compared to concentrations of metals in the mainstem (table 2), although mining has historically occurred to varying degrees in the watershed of many streams in the Clark Fork basin. The low concentrations of metals in the bed sediments of Rock Creek and the Blackfoot River were also consistent with their small contribution to the metal loads in the mainstem (table 3). Only the Pb and Cd concentrations in Flint Creek bed sediment, presumably originating from the historic mining in the headwaters of the basin, are significant compared to metal concentrations in the upstream reach of the Clark Fork basin. Concentrations of Pb in Flint Creek bed sediment are comparable to or exceed those at the confluence with the Clark Fork (table 2; see also Axtmann and others, 1997). Both concentrations and loads point to the existence of significant Pb contamination in Flint Creek. Thus, inputs of sediments from Flint Creek do not dilute Pb concentrations in the Clark Fork bed sediments, and could increase the distance downstream that Pb enrichment extends (Axtmann and others, 1997). This is also true to a lesser extent for Cd which, although slighter lower in concentration that in the mainstem, is sufficiently elevated to extend the distance of enrichment downstream. With the exception of Flint Creek, sediment inputs from the other major tributaries dilute metal concentrations in the suspended and bed sediments of the Clark Fork.

Spatial Patterns in the Mainstem. A consistent downstream decrease in Cd and Cu concentrations was evident in the fine-grained bed sediments of the stations in the monitoring network for every year sampled during the 1986-1995 period (figs. 21 and 22). The same spatial pattern has been reported in previous studies of Silver Bow Creek and the Clark Fork (Andrews, 1987; Axtmann and Luoma, 1991; Brooks and Moore, 1989; Axtmann and others, 1997). The highest concentrations of both Cd and Cu always occurred above the Warm Springs Ponds at Silver Bow Creek at Opportunity. Cadmium and Cu concentrations are substantially lower immediately downstream of the Warm

Springs Ponds, but then nearly double in concentration over the next 5 km to the Clark Fork near Galen, (figs. 21 and 22). With the exception of this anomaly immediately below the Warm Springs Ponds (see later discussion), metal concentrations decreased exponentially downstream from Silver Bow Creek (Axtmann and others, 1997), but did not reach the low levels found in the reference tributaries, even at the farthest downstream site (figs. 21 and 22). At the Clark Fork below Missoula, Cd and Cu concentrations in bed sediments had declined to <5 percent of the concentrations in Silver Bow Creek at Opportunity, but remained approximately 5 -10 fold higher than concentrations found in the least contaminated tributaries (figs. 21 and 22). The similarity of the spatial pattern among years confirms that the decreasing downstream metal concentration gradient is a stable feature of the Clark Fork.

Variability in Metal Concentrations. The range of metal concentrations in bed-sediment samples from some sites was large (fig. 23). In order to detect trends over time, the types and degrees of variability in the data need to be considered. Types of variability include within-site variability, which can be quantified from replicate samples collected at the same time from one site, and interannual variability, which can be quantified from differences in annual mean values for replicate samples collected at one site. The combined variability among all the years sampled during 1986-95 was compared with variability among replicate samples within years, as illustrated for a representative single year (1993). The range, standard deviation, coefficient of variation (CV), and median for both data sets are shown in figure 23. Coefficients of variation, defined as the ratio of the standard deviation to the mean (Zar, 1984), were calculated for each year at each station to determine the within-site variability. The 1993 ratios, as an example, are expressed as percentages at each site (fig. 23).

The average within-site CV's for all years for Cd and Cu were less than 10 percent at Goldcreek, Clark Fork below Drummond and Clark Fork below Missoula (Cd:5.8 percent, 8.6 percent, 7.7 percent respectively; Cu:6.0 percent, 7.6 percent, 5.5 percent, respectively), similar to 1993. The average within-site CV's for all years for Cd at Galen, Deer Lodge and Turah were slightly higher (16.8 percent, 13.2 percent, 18.0 percent, respectively). Within-site variability in Cu concentrations were also higher at Galen, Deer Lodge and Turah (15.8 percent, 25.2 percent, 14.8 percent). The large CV at Deer Lodge is due in part to the large 1991 annual mean Cu concentrations (4183 ±4489μg/g), presumably a reflection of localized metal inputs at the previous sampling location that caused irregular distribution of metal in bed sediments.

Interannual variability in Cd and Cu concentrations in fine-grained bed sediments for all data combined for 1986-95 was greater than within-site variability for individual years, as illustrated by 1993 (fig. 23). For both metals, the within-site CV's were less than the CV's among years at every site, indicating that the differences among years is greater than the variability among replicate samples from a given year. For example, between 1986 and 1995, mean Cd concentrations in bed sediments at Galen ranged from 7.5 μg/g to 20 μg/g, and the CV was 33 percent. However, among replicate samples collected in 1993 at Galen, the range of Cd concentration was 12 -15 μg/g and the CV was 9 percent. The low variability within a year serves to both confirm the spatial differences among sites and to strengthen the likelihood that differences among years are real.

Patterns of Temporal Variability. During 1986-95, temporal changes in Cd and Cu concentrations of bed-sediments occurred only at Galen (figs. 24 and 25). No statistically significant differences in Cd and Cu concentrations were evident among years at the mainstem sites downstream from Galen (figs. 24 and 25). Mean Cd concentrations at Galen in 1991-95 (post-remediation) were all lower than the mean concentration observed in 1987 (pre-remediation), but only the values in 1991 and 1995 were significantly different from 1987 (one-way ANOVA: $p<0.01$).

Considering the large interannual variability, defining pre-remediation conditions from only one year (1987) of data means that any conclusions about post-remediation changes should be viewed with some degree of caution. Concentrations of Cu in bed sediment at Galen were generally similar to patterns for Cd, with significantly higher concentrations in 1987 than in 1991-92 and 1994-1995 (one-way ANOVA: $p<0.01$). The Cu concentration in 1993 was not significantly different from the 1987 concentrations. No trends in Cu concentrations were evident through time at the mainstem sites downstream from Galen (fig. 25).

From 1986 to 1991, bed sediments at Deer Lodge were collected approximately 3 km upstream from the current monitoring site. Exceptionally high and variable Cu concentrations were observed in the bed sediments at Deer Lodge in 1987 and 1991 (2763 $\mu g/g$ and 4183 $\pm$ 4489 $\mu g/g$ respectively; Axtmann, unpublished data). These could have reflected highly variable local influences at the original site.

Relation Between Cu Concentrations in Suspended and Bed Sediment. Annual Cu concentrations in mainstem bed sediments were strongly correlated with estimated annual mean Cu concentrations in suspended sediments ($p<0.01$) (fig. 26). Annual mean concentrations of Cu in suspended sediment (Appendix A) were calculated by dividing the annual suspended Cu load (difference between annual loads of total-recoverable and dissolved Cu) by the annual load of suspended sediment. Metal concentrations in suspended sediment were only calculated for Cu because dissolved concentrations of other metals were commonly below detection, which prevented calculation of the dissolved load. A description of load calculations for dissolved Cu is presented in Appendix A. The relationship indicates that annual variations of the mean Cu concentrations in suspended sediment could be one of the factors controlling Cu concentrations in fine-grained bed sediments measured during summer low-flow conditions (August).

The Cu concentrations observed in 1987 and 1991 in the bed sediments collected at Deer Lodge were significantly higher than expected from the relation with suspended Cu shown in figure 26. As noted above, this is likely to be the effect of localized inputs to the bed from slickens, bank erosion, or ground water at the original Deer Lodge site. Those data were not included when the coefficient of determination was calculated in figure 26. However, the large differences in concentration that occurred when sites were changed illustrates the need for careful coordination of bed-sediment and suspended-sediment sampling locations, especially in the upstream segment of the river.

The regression of annual mean Cu concentrations in suspended sediments against Cu in bed sediments was highly significant during the years of higher streamflow (fig. 26; 1986, 1993 and 1995). During most years of lower streamflow, Cu concentrations in bed sediments were lower than mean annual Cu concentrations in the suspended sediments, excluding 1987 and 1991 at Deer Lodge (fig. 26). Differences between suspended metal concentrations and bed metal concentrations might be indicative of as yet undetermined geochemical or physical processes that differ in importance with flow conditions.

A downward trend in Cu concentrations for both suspended and bed sediments at Galen was indicated when annual mean concentrations were aggregated for the study periods 1985-90 and 1991-95 (fig. 27). The differences in average concentration between study periods were statistically significant (one-way ANOVA: $p<0.01$), although only one year of bed-sediment data was available for the 1985-90 period. Copper concentrations in suspended and bed sediments at Turah were lower in 1991-95 than in 1985-90, but the differences were not statistically significant. The pattern of change in bed sediment Cu concentrations between the two study periods is similar to the downward shift in Cu loads relative to suspended-sediment loads observed during 1991-95 (fig. 10).

Effect of Grain Size Variation in Bed Sediment. Metal concentrations typically increase in the finer fraction of sediments or as the mean grain-size of sediment becomes less coarse (Andrews, 1987; Brooks and Moore, 1989 show data specific to the Clark Fork). Consequently, if grain-size distributions vary among sediment samples, the comparison of metal concentrations may be less informative and mask detection of spatial gradients. Size separation (sieving) of the bed sediment sample is one of the methods recommended to reduce influences on concentration caused by grain-size (Salomons and Forstner, 1984).

Concentrations of Cd and Cu in bulk bed sediments (< 10 mm) were compared to concentrations in fine-grained sediments ($<64\mu m$) at the mainstem sites (fig. 28) to assess the effects of the variable substrate sizes on metal concentrations and variability. In both fine-grained and bulk sediments, median Cd and Cu concentrations were about 2-3 times higher in the fine-grained sediments compared to the bulk sediments at all sites (fig. 28). The downstream decrease in concentrations in the fine-grained sediments had a more uniform gradient than that in the bulk sediments. Within-site variability in Cd and Cu concentrations in bulk sediments (expressed as the coefficient of variation, CV) was inconsistent between sites and commonly higher, sometimes substantially, than in the fine-grained sediments. Thus, sieving enhanced the detection of spatial differences and should increase the likelihood of detecting temporal trends by minimizing the variance caused by particle-size differences between bed-sediment samples.

Biota

Tributaries. Insect larvae were collected from tributaries for whole-body metal analysis as a reference to concentrations and temporal trends in the mainstem (table 2). Concentrations of Cd, Cu, and Pb in the caddisfly, *Hydropsyche cockerelli,* were greater in the Little Blackfoot River and Flint Creek than in Rock Creek and the Blackfoot River. This pattern of enrichment was similar to that for bed sediments in these four tributaries (table 2), suggesting that metal concentrations in sediments and bioaccumulation within the food chain are both responsive to metal inputs. *H. cockerelli* was not present in Warm Springs Creek near its confluence with the Clark Fork, but the predominant caddisfly in that stream (*Arctopsyche grandis*) had elevated concentrations of Cd, Cu, and Pb compared to Rock Creek and the Blackfoot River (see Dodge and others, 1996 for Rock Creek and Blackfoot River data).

Spatial Patterns in the Mainstem. The spatial pattern of Cd and Cu concentrations in *H. cockerelli* follows a decreasing downstream trend (figs. 29 and 30), generally similar to that observed for bed sediments. Concentrations of Cd and Cu decreased downstream in the pattern reported by Cain and others (1992), in every year of the 1986-1995 period. Highest concentrations of both Cd and Cu always occurred above the Warm Springs Ponds in Silver Bow Creek at Opportunity (figs. 29 and 30). The lowest metal concentrations in the upstream reach were observed directly below the ponds in Silver Bow Creek at Warm Springs. Concentrations of Cd and Cu increased within 4 km below the ponds (at Galen) as local metal sources apparently became more available. Concentrations generally decreased downstream from Galen.

Metal concentrations in *H. cockerelli* from the upper and middle reaches of the Clark Fork were always higher than in *H. cockerelli* from Rock Creek and the Blackfoot River (table 2). The lowest concentrations in the mainstem were observed 280 km downstream, at the Clark Fork below Missoula. Concentrations in *H. cockerelli* at this site were higher than concentrations in the tributaries in most, but not all years.

Variability in Metal Concentrations. Within-site variability in Cd and Cu concentrations was low among replicate composite samples collected in each year, partly because of the large numbers of individual insects composited for each analysis. The coefficient of variation (CV) for each year at each station was calculated to determine the within-site variability. A single year (1993) was used to illustrate the comparison of typical within-site variability to interannual variability (fig. 31). The average within-site CV for all years for Cd at Galen, Deer Lodge and Goldcreek was less than 10 percent (8.3 percent, 7.3 percent, and 8.3 percent, respectively). The average CV's at Clark Fork below Drummond, Turah and Below Missoula were slightly higher (13.7 percent, 12.3 percent, and 10.7 percent, respectively). Cd concentrations among replicate samples were slightly more variable below Flint Creek, suggesting the possibility that inputs from the Flint Creek may have some effect on Cd concentrations in the mainstem. The average CV in Cu concentrations for all years at each station (fig. 31) was also low, with Galen, Goldcreek, and below Drummond being less than 10 percent (8.3 percent, 5.2 percent and 2.4 percent respectively); although, the within-site variability at Deer Lodge, Turah and below Missoula were slightly higher (11.2 percent, 12 percent, and 13.4 percent, respectively).

Interannual variability in Cd and Cu concentrations in *Hydropsyche* for all data combined between 1986-95 was substantially greater than within-site variability for individual years (fig. 31). The CV's for Cd ranged from 28-54 percent and were higher than the CV's for Cu in the middle reach of the river and at Turah Bridge (range of 19-42 percent). The interannual CV's were similar for both metals at Galen and Deer Lodge.

Patterns of Temporal Variability. Concentrations of Cd and Cu in insects at mainstem sites from Galen to below Missoula show no clear evidence of trends through time (figs. 32 and 33). Differences between pre- and post-remediation also were not always evident. At all sites where data were available, concentrations of Cd and Cu in 1986 and 1987 (pre-remediation) were among the highest observed during the 1986-95 study period. Cadmium concentrations in 1993 were nearly equal to the concentrations in 1986-87 (figs. 32). Years of maximum Cu concentrations during 1991-95 were variable and not distinctly different from available pre-remediation data, with the exception of Deer Lodge, where the sampling location was moved (fig. 33). The intermittent data base prior to 1991 may preclude any conclusive evidence of temporal trends.

Processes Affecting Bioaccumulation: Upstream Reach. Four monitoring sites along an approximate 50 km reach from Silver Bow Creek at Opportunity (-13.8 km), to the Clark Fork at Deer Lodge (44.6 km) were sampled in 1992 (table 6), to specifically study the general concentration gradient in the upper Deer Lodge valley. Additional sites below the Warm Springs Ponds were sampled in 1993 to provide spatial detail on this reach closest to the ponds. Table 6 summarizes the annual mean metal concentrations in fine-grained bed sediments and in *H. cockerelli* in the most upstream reach of the river.

In all years, concentrations of Cd and Cu in insects and bed sediments throughout this upstream reach were lower than concentrations at Silver Bow Creek at Opportunity (table 6). Cadmium concentrations in *H. cockerelli* at Silver Bow Creek at Warm Springs (-2.1 km) and at a site on the Clark Fork below Warm Springs Creek (0.5 km) were 13 - 32 percent of the concentrations observed in Silver Bow Creek at Opportunity (0.6 - 2.0 μg/g vs. 4.6-6.3 μg/g). Copper concentrations decreased similarly below the Warm Springs Ponds and were 13 - 22 percent of the concentrations at Opportunity (37 -97 μg/g vs. 295-439 μg/g). Cadmium concentrations in bed sediment in Silver Bow Creek at Warm Springs (-2.1 km) and Below Warm Springs Creek (0.5 km) were 22 - 32 percent of the concentrations observed in Silver Bow Creek at Opportunity (6.0 -12.2 μg/g vs. 27.1 - 38.2 μg/g). Copper concentrations in bed sediment were 6 - 22 percent of those in Silver Bow Creek at Opportunity (259 - 1360 μg/g vs. 4560-6280 μg/g).

Two additional sites were sampled in 1993 on Silver Bow Creek in the short reach between Silver Bow Creek at Warm Springs (-2.1 km) and Warm Springs Creek (0.5 km). Concentrations of Cd and Cu in *H. cockerelli* at all four sites were similar (table 6), verifying that the reduced concentrations below the ponds were not just site-specific observations. The spatial distributions of Cd and Cu concentrations in fine-grained bed sediments were more variable than those in the *H. cockerelli* among the four sites (table

Table 6: Annual mean Cd and Cu concentrations in fine-grained bed sediment and Hydropsyche cockerelli in the upper reach of the Clark Fork Basin.

		Cd in H. cockerelli (ug/g)				*Cu in H. cockerelli (ug/g)*			
Station (Km)	**River Km**	**1992**	**1993**	**1994**	**1995**	**1992**	**1993**	**1994**	**1995**
Silver Bow Creek at Opportunity	-13.8	4.6	—	4.6*	6.3	397	—	295*	439
Silver Bow Creek at Warm Springs	-2.1	0.9	2.0	1.5	0.6	58.0	96.9	51.9	36.9
Silver Bow Creek near Warm Springs	-1.6	—	1.7	—	—	—	82.8	—	—
Silver Bow Creek below Warm Springs	-0.6	—	1.8	—	—	—	96.2	—	—
Clark Fork below Warm Springs Creek	0.5	—	1.1	1.2	1.1	—	74.5	92.9	85.3
Clark Fork near Galen	4.7	2.4	2.6	1.7	1.5	177	176	100	89.7
Clark Fork at Deer Lodge	44.6	0.8	1.6	1.4	1.3	60.0	81.8	113	104

		Cd in Sediments (ug/g)				*Cu in Sediments (ug/g)*			
Station (Km)	**River Km**	**1992**	**1993**	**1994**	**1995**	**1992**	**1993**	**1994**	**1995**
Silver Bow Creek at Opportunity	-13.8	27.1	29.3	38.2	36.7	4560	4570	5020	6280
Silver Bow Creek at Warm Springs	-2.1	8.2	12.2	10.6	6.0	536	769	716	259
Silver Bow Creek near Warm Springs	-1.6	—	22.2	—	—	—	1279	—	—
Silver Bow Creek below Warm Springs	-0.6	—	24.7	—	—	—	2461	—	—
Clark Fork below Warm Springs Creek	0.5	—	12.3	10.0	7.4	—	1358	1069	779
Clark Fork near Galen	4.7	15.2	13.2	11.9	7.5	1266	1520	1230	1220
Clark Fork at Deer Lodge	44.6	8.3	5.6	6.3	9.0	1043	992	882	1480

*Hydropsyche morosa group is reported here. Hydropsyche cockerelli is in the morosa group, but it could not be positively identified to species level.

6). Concentrations of Cd in the bed sediment at the intermediate sites are nearly 100 percent higher than concentrations directly above and below Warm Springs Creek (22.2-24.7 μg/g Cd vs. 12.3 μg/g). Copper concentrations were 55-60 percent higher in the intermediate sites than concentrations found in Silver Bow Creek at Warm Springs and Below Warm Springs Creek (769-1358 μg/g vs. 1279-2461 μg/g).

The reach of reduced concentration below Warm Springs Ponds was relatively short. In 1993, concentrations of Cu in insects doubled and concentrations of Cd increased three-fold between Below Warm Springs Creek (0.5 km) and the Clark Fork near Galen (4.7 km) (table 6, figs. 34 and 35). Concentrations of Cd and Cu also increased in bed sediments during 1993-95, verifying conclusions from the load data that substantial metal inputs occur in the reach between Warm Springs Ponds and the Clark Fork near Galen. Thus, the decrease in metal enrichment provided by the Warm Springs Ponds was partially offset by local sources of metal input within a few kilometers, although the resulting concentration at Clark Fork near Galen remained well below that above the ponds in Silver Bow Creek at Opportunity.

Lower concentrations of Cd and Cu in *H. cockerelli* and in bed sediment occur at Deer Lodge than at Galen in most years (fig. 34, table 6). In 1992 and 1993, Cd concentrations in *H. cockerelli* at Deer Lodge were lower than concentrations at Galen (0.8 vs. 2.4 μg/g in 1992, and 1.6 vs. 2.6 μg/g in 1993). Copper concentrations were 60 vs.177 μg/g in 1992 and 81.8 vs. 176 μg/g in 1993, respectively.

Concentrations of Cd and Cu in bed sediment also showed similar trends (fig. 35). Cadmium concentrations in bed sediment at Deer Lodge in 1992-93 (8.3 and 5.6 μg/g, respectively) were 2-3 times less than the Cd concentrations at Galen (15.2 vs. 13.2 μg/g). Copper concentrations at Deer Lodge in 1992-93 (1043 and 992 μg/g, respectively) were also lower than Cu concentrations at Galen (1266 and 1520 μg/g) (table 6).

In 1994 and 1995, Cd and Cu concentrations at Galen in *H. cockerelli* were 58 percent - 71 percent of the concentrations in 1992-93 (table 6). If these differences continue, then a zone of reduced metal concentration below the ponds may be expanding downstream to Galen as a result of remediation. However, concentrations of Cd and Cu in 1994-95 at Galen were not statistically different than from those observed in 1991. Thus, at this point in time, the large year-to-year variability characteristic of this upstream reach, and the paucity of systematic data from before 1992, make any conclusive interpretation of temporal trends tenuous.

Concentrations of Cu in *H. cockerelli* for individual years were plotted against several annual mean environmental parameters to examine, at each site, the relationship of factors that may affect metal transfer to insects. Copper in *H. cockerelli* was regressed against annual streamflow, annual total-recoverable Cu load, annual dissolved Cu load, Cu concentrations in suspended sediment, and Cu concentrations in fine-grained bed sediment.

No significant correlations between Cu concentrations in *H. cockerelli* and the physical or chemical variables were evident at Galen (fig. 36). The lack of correlation and the high variability among years both indicate that highly variable local sources or geochemical processes, may influence metal uptake at Galen.

A significant positive correlation ($p<0.01$) between Cu concentrations in *H. cockerelli* and annual dissolved Cu load occurs at Deer Lodge (fig. 37) and suggests that the dissolved concentrations of Cu at the station may be at least in part responsible for the uptake by *H. cockerelli*. A significant inverse relationship ($p<0.001$) occurs with Cu concentrations in *H. cockerelli* and estimated Cu concentrations in suspended sediments (fig. 37).

In summary, two of the integrated measures employed in this study, annual Cu discharge relative to sediment discharge (Cu:sediment ratios) and annual mean Cu concentrations in suspended sediments, showed initial indications that Cu concentrations may have declined at Galen during the post-remediation period (1991-95, although hydrologic effects likely contribute to this temporal pattern. Sampling of bed sediment and *H. cockerelli* between the Warm Springs Ponds and Galen in 1992-93 a similar pattern of declining metal concentrations. However, year-to-year variability is substantial in this upstream reach. Because this variability is influenced by as yet unexplained, possibly local processes, remediation-induced trends will be difficult to separate from natural variability. Continued integrated monitoring of metals using several environmental indicators will be necessary to better determine the validity of the initial indications of trends and mechanisms.

Processes Affecting Bioaccumulation: Middle Reach. Metal concentrations at the uppermost mainstem site of the middle reach, Clark Fork at

Goldcreek, reflect the cumulative effects of processes occurring in the upstream reach. Slickens and visibly contaminated banks are less common in the middle reach, so the influences of local inputs could be less than in the upstream reach near Galen and Deer Lodge.

Water-quality data was not collected before 1993 at Goldcreek, but streamflow has been gaged since 1977 and was used as a surrogate for metal discharge during the 1986-95 period (figs. 38 and 39). Strong correlations between annual streamflow and concentrations of Cd (R^2=.85; p<0.001) and Cu (R^2=.69; p<0.01) in *H. cockerelli* were observed. The significant correlations indicate that the year-to-year variability of metal uptake by *H. cockerelli* is driven in part by hydrologic influences. Dissolved Cu concentrations, estimated Cu concentrations in suspended sediments, and Cu concentrations in bed sediments did not correlate significantly with Cu concentrations in *H. cockerelli*, within the small set of available data.

In the middle reach, substantial variability in bioavailable metal inputs among years appears to be partly explained by variable hydrology, as best indicated by the significant Cd and Cu correlations with annual streamflow. The mechanistic reason for this relationship is not yet clear, but the initial correlation between bioaccumulated metal and streamflow could provide a baseline for evaluating future trends in metal concentrations in the insects relative to the correlations for 1986-1995 at Goldcreek.

Processes Affecting Bioaccumulation: Downstream Reach. Metal concentrations at the first mainstem site in the downstream reach, Clark Fork at Turah Bridge reflect the cumulative effects of processes occurring in the entire watershed above, including the major tributaries Flint Creek and Rock Creek. Metal enrichment of bed sediments, suspended sediments, and *Hydropsyche cockerelli* indicate that the Clark Fork at Turah has been affected by the input of metal in the upper basin. However, understanding processes by correlating various environmental indicators could be difficult because concentrations are lower than in the middle or upper reaches (due to greater distance from headwater metal sources and dilution from tributaries). Basinwide factors such as geology or land-use may also exert proportionally more influence on metal trends and behavior than at upstream stations.

Annual mean concentrations of Cu in *H. cockerelli* at Turah varied less than two-fold (27 to 44 μg/g), while the relative range in total-recoverable and dissolved Cu loads varied five to ten-fold (fig. 40). Estimated annual mean concentrations of Cu in suspended sediments varied less than two-fold. None of the physical or chemical variables correlated significantly with Cu concentrations in *H. cockerelli*. Most notably, no relationship was apparent between annual streamflow and Cu concentrations in *H. cockerelli* (fig. 40), a distinct difference from Goldcreek.

Cadmium concentrations in *H. cockerelli* varied four-fold in contrast to the less variable Cu concentrations (fig. 41). Annual patterns of variability in Cd concentrations were similar to the sites in the middle reach of the river, although at lower concentrations (fig. 32). Cadmium concentrations for 1986-1995 in *H. cockerelli* from Clark Fork at Turah Bridge correlated significantly with total annual streamflow (R^2=0.71). The correlation is greatly influenced by high bioavailable Cd in concentrations in some years of high streamflow. The correlation was similar to, but not as strong as, that observed at Goldcreek.

The reasons for the differences in the correlation to annual streamflow between Cd and Cu at Turah are not yet clear. One possibility is that the Cd available for bioaccumulation is more geochemically mobile than Cu in the watershed, resulting in transport further downstream. A second possibility is that additional inputs of Cd from Flint Creek or other sources contribute to the Cd load more than the Cu load. However, because Cd loads cannot be accurately estimated due to low concentrations, additional years of data are necessary to identify temporal trends of Cd and Cu in insects in order to detect differences that could infer a Cd source.

SUMMARY AND CONCLUSIONS

This report describes the spatial distributions and temporal trends of metals in water, bed sediment, and biota of the upper Clark Fork basin during 1985-95. Possible trends are examined relative to hydrologic conditions during the period. A sampling network for surface water was established by the USGS in 1985 in the upper Clark Fork basin above Missoula. Bed-sediment and aquatic insects were sampled independently at several of the surface-water sites in 1986-92. In 1993, bed-sediment and biological sites were integrated with the surface-water sites to establish a basinwide network for systematic, long-term sampling. The primary purpose of the monitoring network is to track the ongoing status of metal concentrations and associated factors that may affect those concentrations. These long-term data can be used to evaluate the effectiveness of remediation on decreasing metal enrichment in the Clark Fork, and ultimately, to provide a basis for determining if cleanup goals for the upper Clark Fork basin have been achieved.

The description of metal characteristics for water, bed sediment, and biota during 1985-95 covers a wide range of hydrologic conditions and establishes reference data that should be useful for interpreting future changes. The multivariate data give insight into how biota respond to changes in the aquatic environment and provide a baseline against which to evaluate trends in the Clark Fork basin related to remediation.

As mitigation proceeds, it will be useful to determine whether conditions in the Clark Fork are improving. Short-term temporal trends in metal enrichment of water, sediments or biota can be caused by varying hydrologic or climatic factors that affect metal inputs or enrichment among years, thereby making detection of remediation effects difficult. In addition, inconsistent sampling methods, location, and season are other factors that can cause variability in data among years. Careful coordination of bed-sediment, suspended-sediment, and biota sampling is essential for collecting internally consistent data to characterize metal in the aquatic environment, especially in the highly variable upstream reach of the river.

In the upper reach of the Clark Fork, variable hydrologic regimes, coupled with inputs from the extensive local sources of metal, contribute to the challenge of determining if remediation is resulting in persistent decreases in metal enrichment. At present, the multivariate data base from the upper reach spans a decade, and includes some data from both pre- (1985-90) and post- (1991-95) remediation periods. The concurrent monitoring of multiple indicators has been in place only since 1992, with less systematically collected data available for 10 years.

Specific processes driving changes in metal concentrations and loads are not fully explained by the available data. The causes of trends or changes should become more clear with time as the natural variability in the system is better understood.

Summarized below are the major conclusions based on analysis of data collected during 1985-95:

- Streamflow has a large influence on year-to-year variability of suspended-sediment and metals transport. Only by examining hydrologic conditions concurrently with metal transport can persistent patterns over time be detected.

- Both the 1985-90 and 1991-95 study periods had maximum flows substantially less than those recorded for the long-term record (1930 - 1995); consequently, suspended-sediment and associated metal loads may have been larger in the past than those measured during 1985-95.

- The metal load transported by the Clark Fork was substantially larger than that contributed from the Blackfoot River. The proportion of metal loads of Cu, Pb, and Zn transported to Milltown Reservoir by the Clark Fork and Blackfoot River were similar during both the 1985-90 and 1991-95 periods.

- The four major tributaries located between Warm Springs Ponds and Turah Bridge (Warm Springs Creek, Little Blackfoot River, Flint Creek, and Rock Creek) contributed only a minor proportion of the total metal discharged from the Clark Fork to Milltown Reservoir. One exception was Flint Creek, which contributed 12 percent of the Pb load discharged to Milltown Reservoir during 1991-95.

- A large proportion of metal input came from the intervening reaches of the Clark Fork between mainstem sampling sites (excluding tributary inputs). The largest single contribution to the cumulative metal load entering Milltown Reservoir was from the 39.9 km reach between the Clark Fork near Galen and the Clark Fork at Deer Lodge (30 percent of the Cu, 17 percent of the Pb, and 17 percent of the Zn during 1991-95). The short 6.8 km reach between Silver Bow Creek at Warm Springs and the Clark Fork near Galen contributed approximately twice the Cu and Zn load of the entire Warm Springs Creek basin during 1991-95. The lower Deer Lodge valley between Deer Lodge and Goldcreek contributed only about 6-10 percent. The intervening reaches between Goldcreek and Drummond, and between Drummond and Turah Bridge, each contributed moderate metal loads (~ 8-19 percent) to Milltown Reservoir.

- On the basis of a unit-length comparison of tons of metal per river km, the greatest linear yield of Cu, Pb, and Zn occurred in the two reaches above Deer Lodge. Copper inputs from these reaches were 3 to 5 times greater per river km than in any downstream reach.

- Graphical analysis of concurrent time series indicated that there was no trend evident in the relative amounts of annual streamflow and suspended-sediment discharge during 1985-95.

- Concurrent plots of annual suspended-sediment and total-recoverable Cu loads for the Clark Fork near Galen and at Turah Bridge, indicate a small downward shift of Cu discharge relative to suspended-sediment during 1991-95 compared to 1985-90. The magnitude of the shift was variable for individual years, but the effects were persistent throughout the entire five years, despite the wide range of hydrologic conditions. A similar shift at several tributaries suggests that basinwide hydrologic processes may contribute to the shift observed at the mainstem sites. There was no downward shift of Cu discharge relative to sediment discharge evident at Deer Lodge during 1985-95. It is possible that Cu sources in the intervening reach between Galen and Deer Lodge are sufficient to mask any decrease in Cu load occurring above Galen. Less distinct patterns occurred for Pb and Zn transport.

- The mass ratio of annual total-recoverable Cu load to suspended-sediment load decreased with increasing annual streamflow at all sites. This relation indicates that greater inputs of non-channel sediment during high-flow years may dilute the Cu content of suspended sediment. The similarity of this pattern in remediated and unremediated areas supports the likelihood that streamflow increases in recent years contributed to downward shifts in Cu:sediment ratios.

- Pre- and post-remediation regression relations for Cu concentration in stream samples indicated little or no statistical difference between 1985-90 and 1991-95. However, dissolved Cu relations for Galen and Deer Lodge showed a weak, but statistically significant, downward shift.

- Metal concentrations in bed sediments and *H. cockerelli* were low in most tributaries compared to concentrations in the mainstem. One exception was Flint Creek, where concentrations of Pb were comparable to those in middle reach of the Clark Fork.

- A decreasing downstream gradient in metal concentrations was evident in the fine-grained bed sediment in every year of study. At the Clark Fork below Missoula, Cd and Cu concentrations were less than 5 percent of those at Silver Bow Creek at Opportunity, but were 5-10 times higher than those in Rock Creek or the Blackfoot River.

- Metal concentrations at every site were higher in fine-grained bed sediments than in bulk bed sediments in 1993-95. Within-site variability in concentrations was decreased by sieving, which clarified spatial distributions of metals in bed sediments.

- Bed-sediment data prior to 1991 are limited, but concentrations of Cd and Cu at Galen were all lower in 1991-95 than in 1987. No persistent pattern over time was evident for either Cd or Cu in bed sediment at mainstem sites downstream from Galen.

- Annual mean Cu concentrations in suspended sediments were strongly correlated with Cu concentrations in fine-grained bed sediments for both high and low flow years.

- Tributaries with metal enrichment in their sediments also were characterized by metal enrichment in *H. cockerelli.*

- The spatial pattern of Cd and Cu concentrations in *H. cockerelli* in the Clark Fork was generally similar to the downstream gradient observed for bed sediments, although concentrations in *H. cockerelli* were considerably lower. From the Clark Fork near Galen to below Missoula, Cd and Cu concentrations decreased by about four- to five-fold. Concentrations in *H. cockerelli* at the Clark Fork below Missoula were higher than concentrations in the tributaries in most, but not all, years.

- At the Clark Fork near Galen, bioaccumulated Cu most closely followed annual mean Cu concentrations in suspended sediment, but did not correlate significantly with other environmental parameters such as streamflow or Cu in bed sediment. Concentrations of Cd and Cu in *H. cockerelli* at Galen were lower in 1994-95 than in 1992-93 and 1987. However, concentrations were also low in 1991, indicating that temporal trends are not yet clear. Local inputs from floodplain sources or hydrologic effects may add substantial variability to metal bioaccumulation at Galen and complicate trend detection.

- Using annual streamflow as a surrogate for 1986-95 metal transport at Goldcreek (where water quality sampling did not begin until 1993), a highly significant positive correlation between annual streamflow and bioaccumulated Cd and Cu existed for the period 1986-95. This relation illustrates the strong influence of annual hydrologic conditions on metal exposure of biota.

- In the Clark Fork at Turah Bridge, concentrations of Cu in *H. cockerelli* were lower than observed at Goldcreek, and showed less variability among years. A significant correlation between annual streamflow and Cd in *H.*

cockerelli was observed at Turah, but no significant correlation was found with Cu.

Only a relatively small data set is presently available for evaluating relationships between multiple environmental parameters and bioaccumulated Cd and Cu. It appears that hydrologic differences among years contribute to year-to-year variability and may influence bioaccumulation. However, the influences are complex and may be site-specific or reach-specific. Similarities in some trends suggest that further data collection may provide insight to mechanisms that can explain these influences and perhaps identify effects from remediation. In such a variable system, understanding year-to-year differences is an essential prerequisite to interpreting trends.

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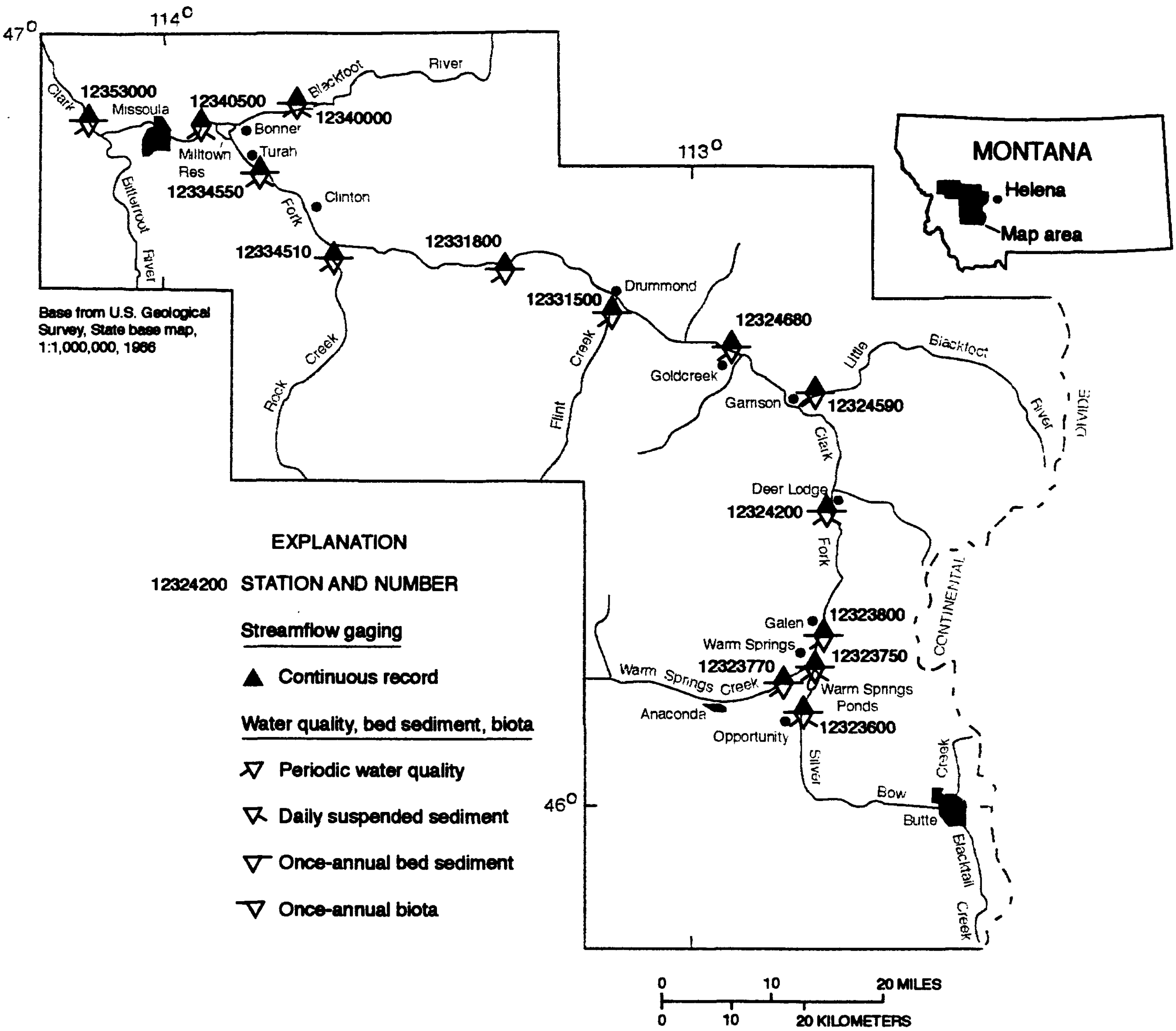


Figure 1. Location of study area.

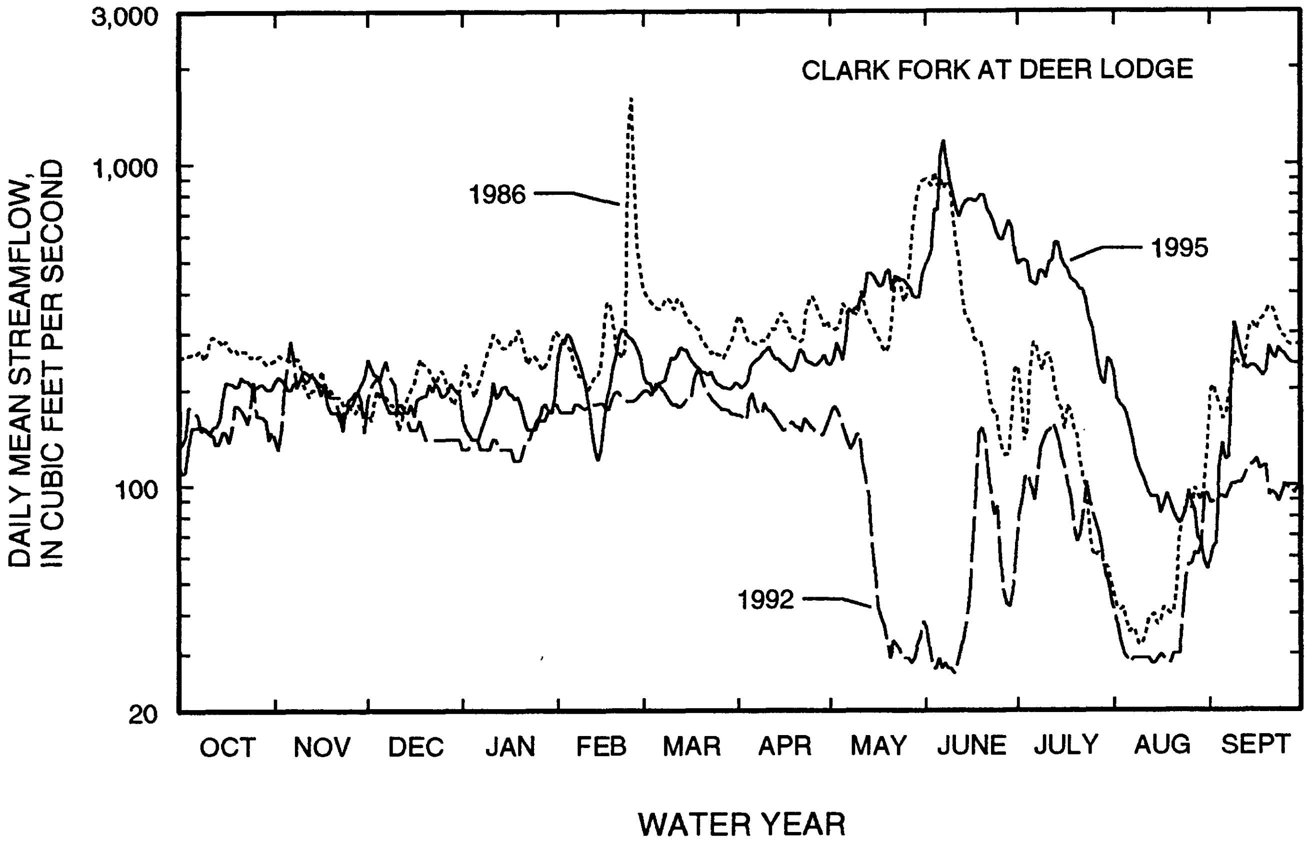


Figure 2. Hydrographs of selected water years for the Clark Fork at Deer Lodge.

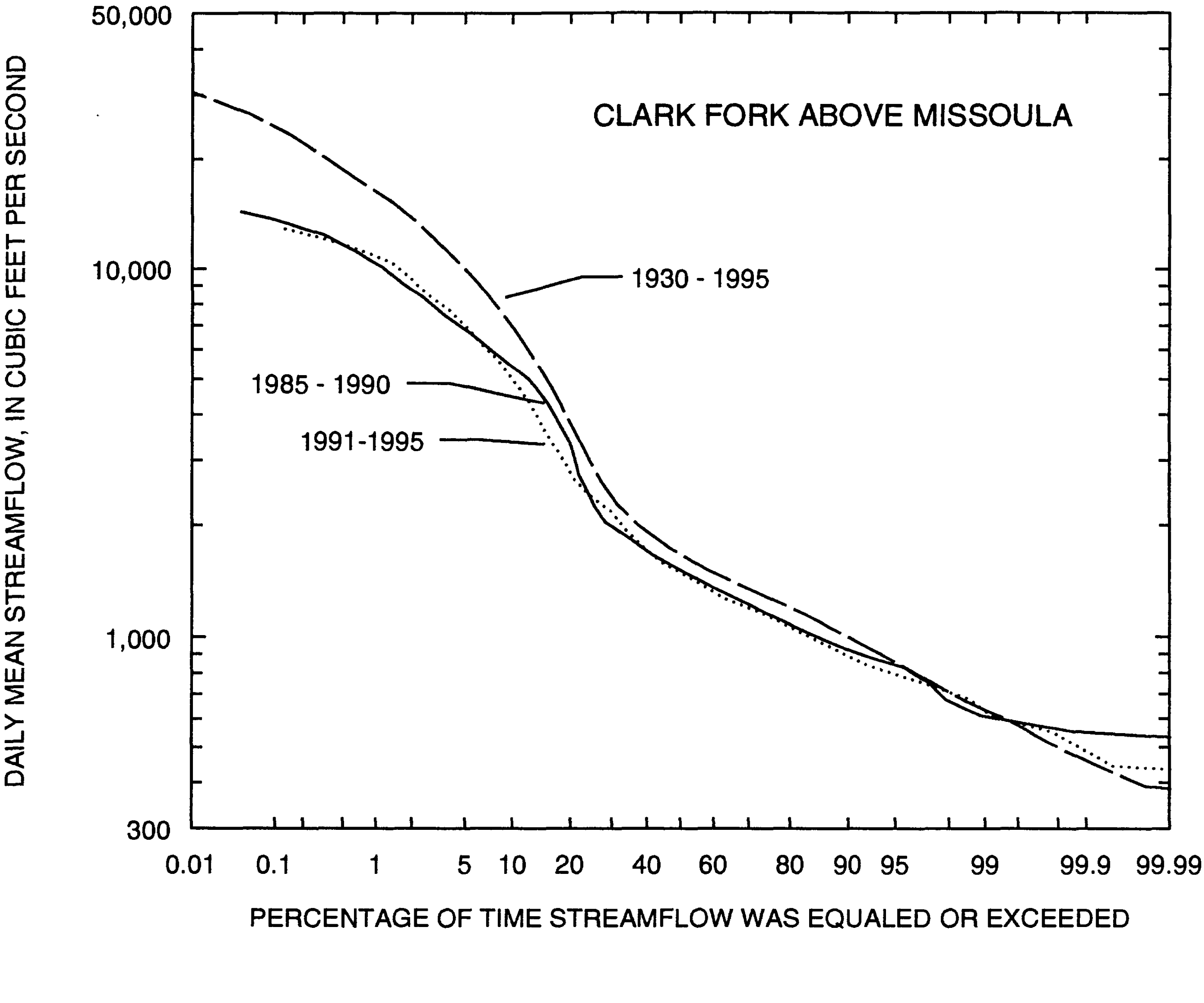


Figure 3. Streamflow-duration curves for the Clark Fork above Missoula during the period of record (water years 1930-95) and recent study periods (water years 1985-90 and 1991-95)

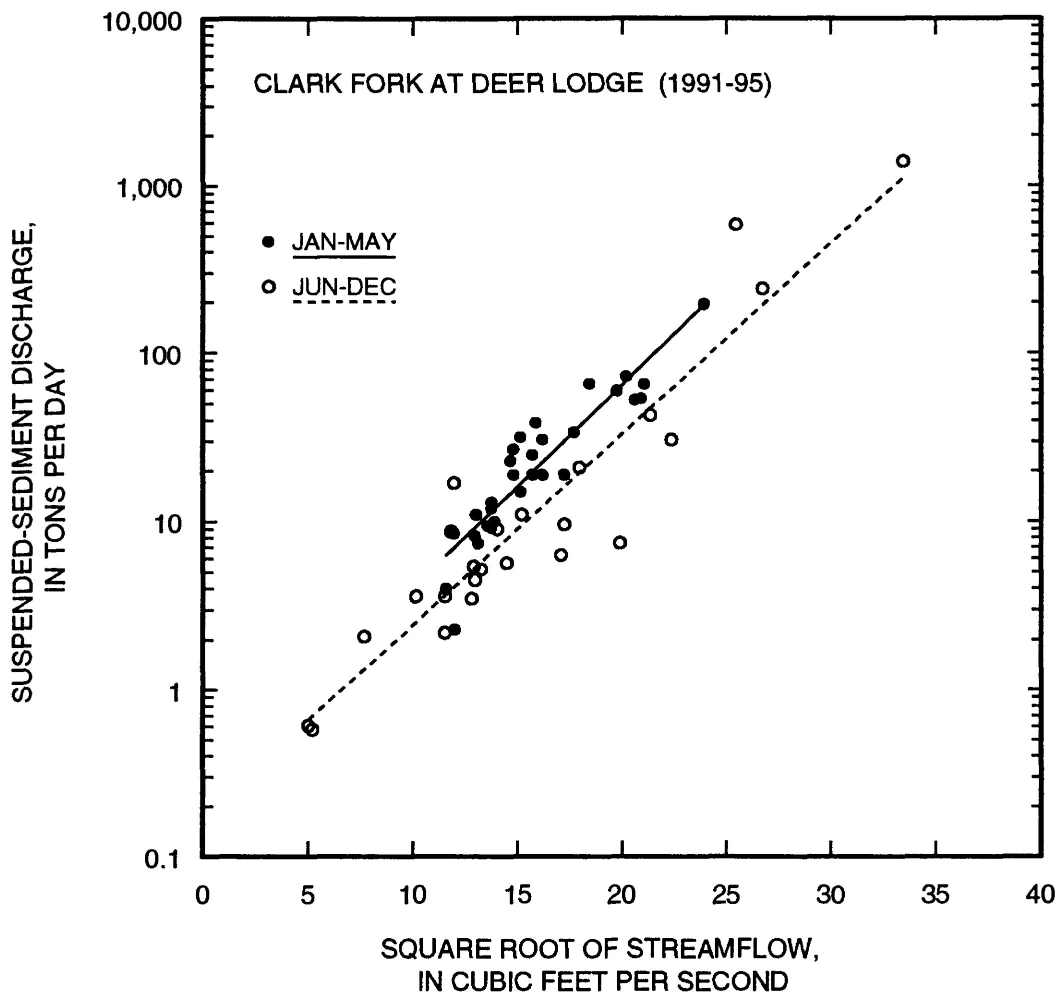


Figure 4. Seasonal relations between streamflow and suspended-sediment discharge for the Clark Fork at Deer Lodge, water years 1991-95.

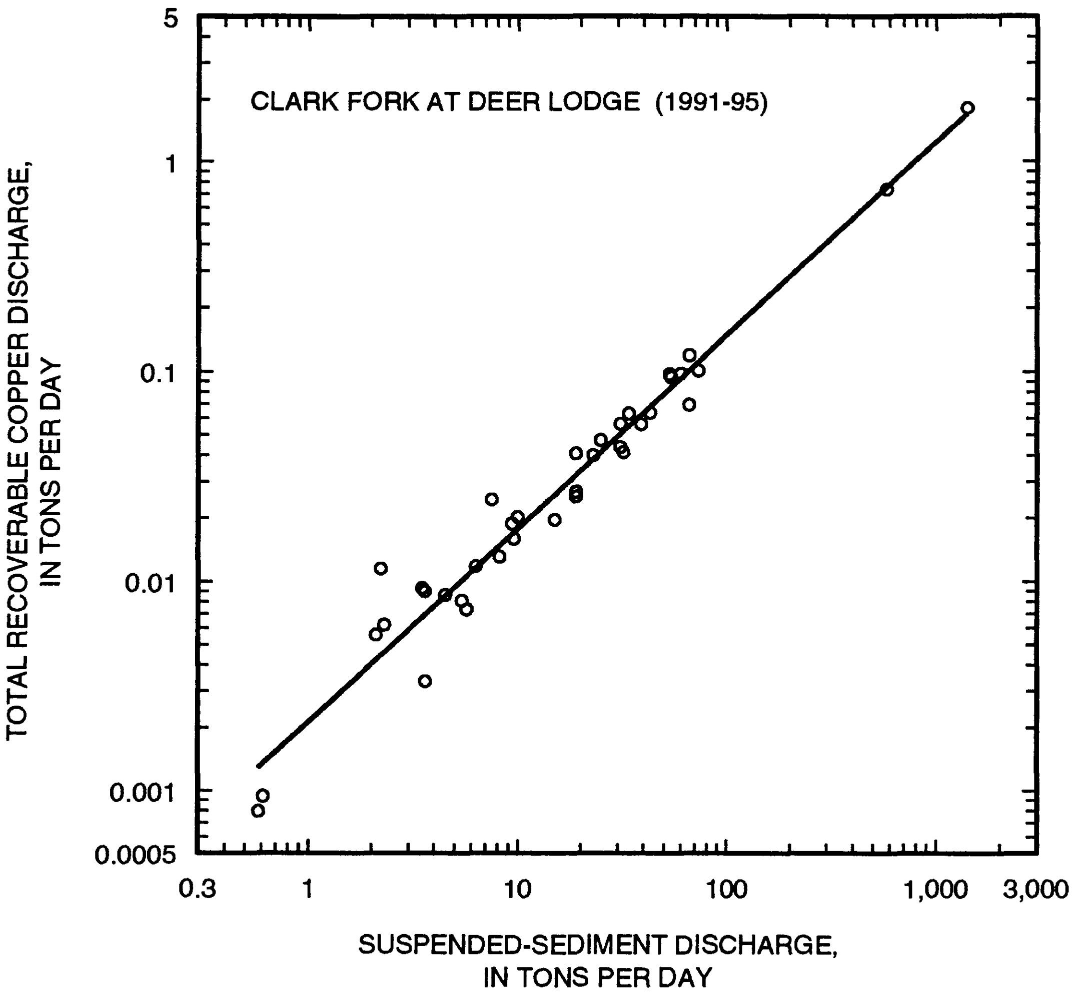


Figure 5. Relation between suspended-sediment discharge and total-recoverable copper discharge for the Clark Fork at Deer Lodge, water years 1991-95.

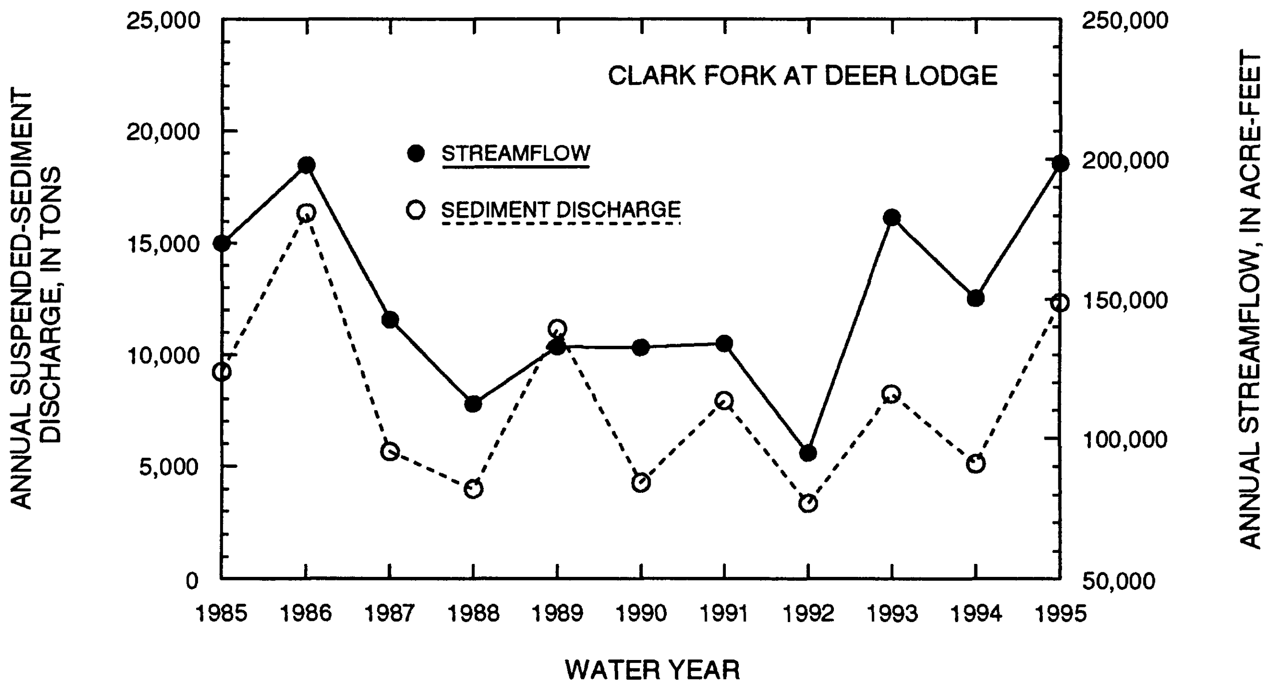


Figure 6. Annual streamflow and suspended-sediment discharge for the Clark Fork at Deer Lodge, water years 1985-95.

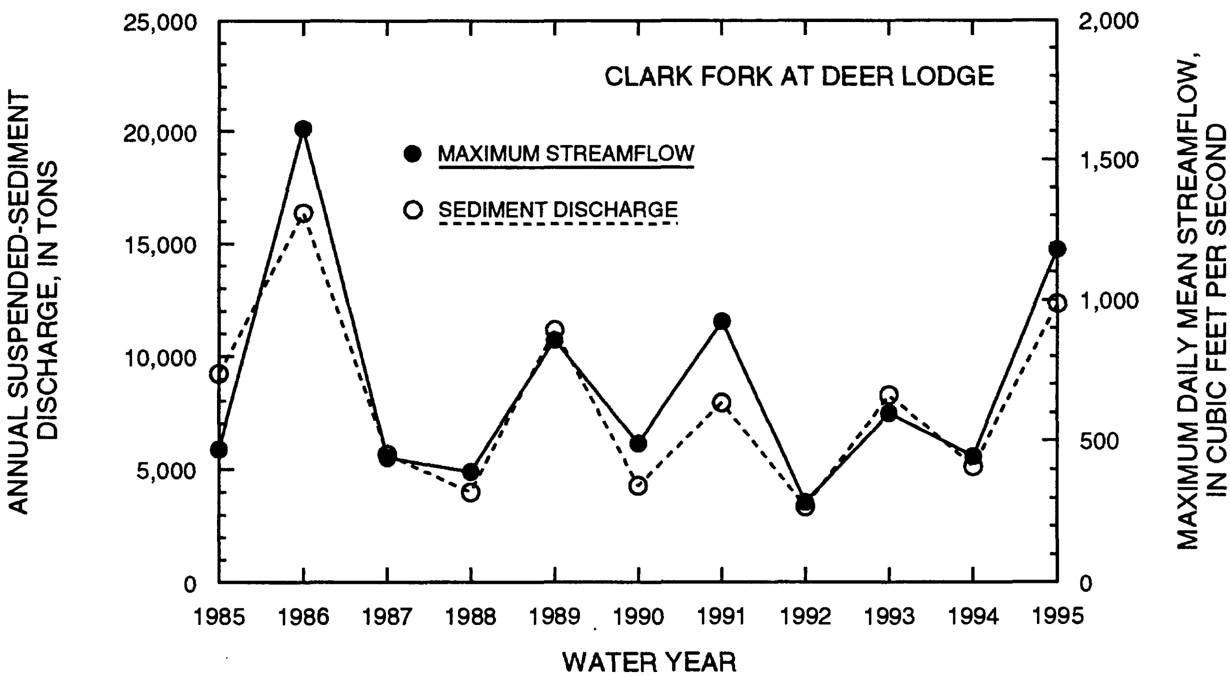


Figure 7. Maximum daily streamflow and annual suspended-sediment discharge for the Clark Fork at Deer Lodge, water years 1985-95.

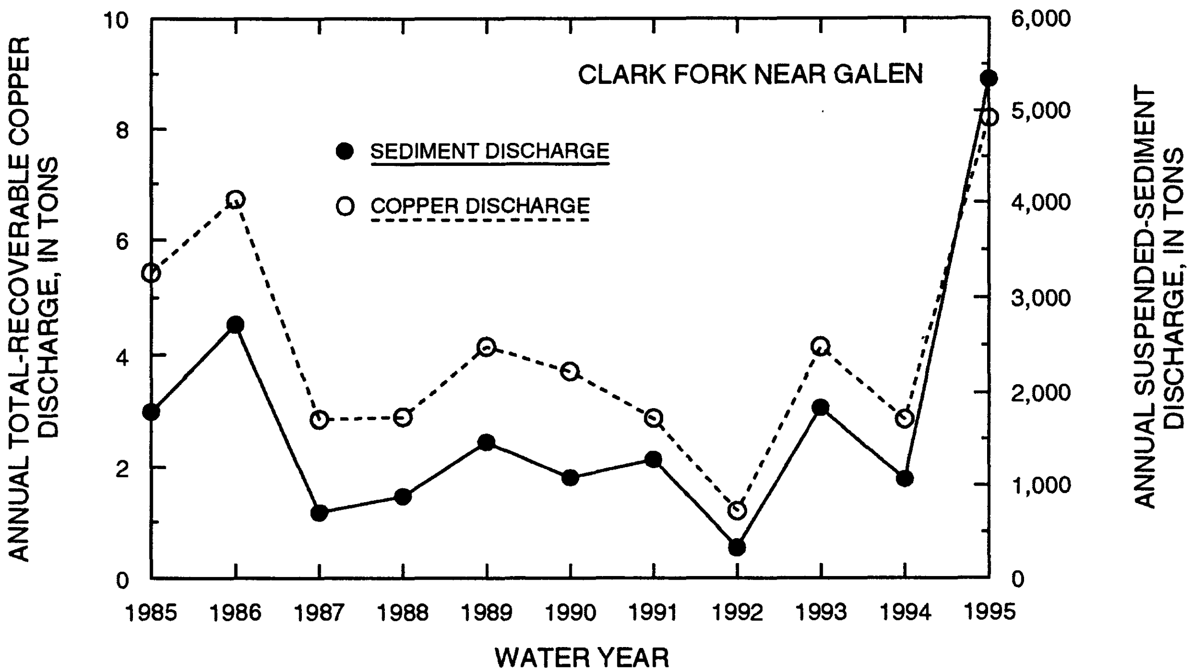


Figure 8. Annual suspended-sediment discharge and total-recoverable copper discharge for the Clark Fork near Galen, water years 1985-95.

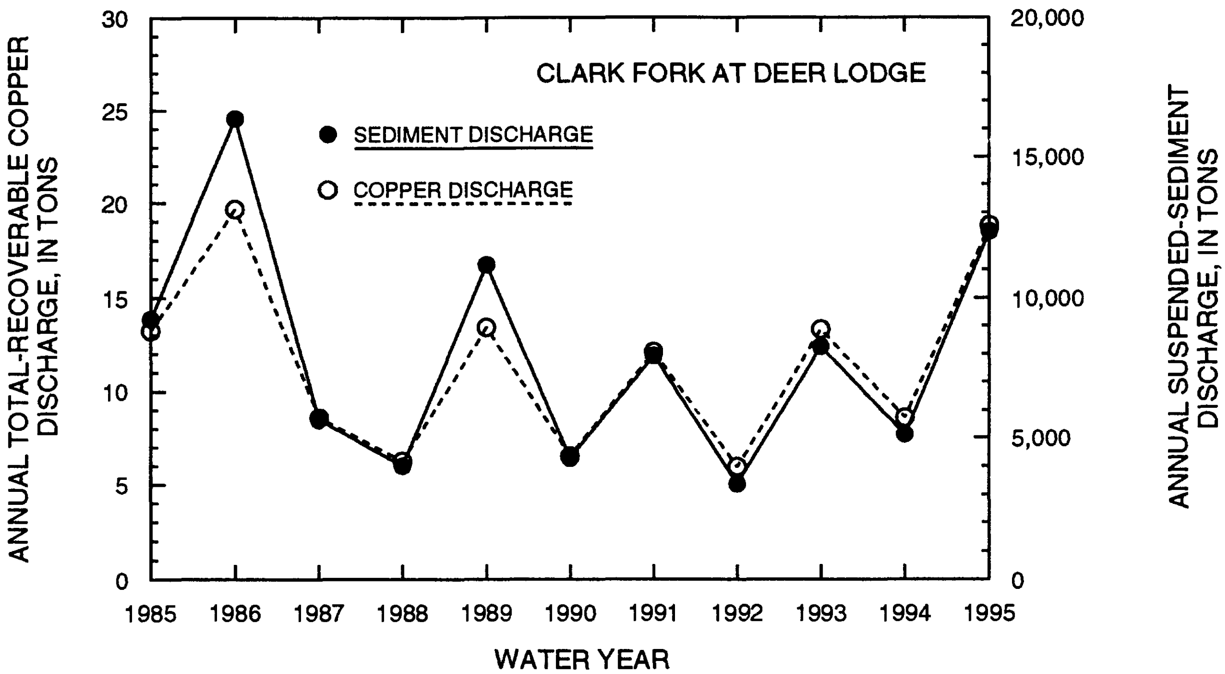


Figure 9. Annual suspended-sediment discharge and total-recoverable copper discharge for the Clark Fork at Deer Lodge, water years 1985-95.

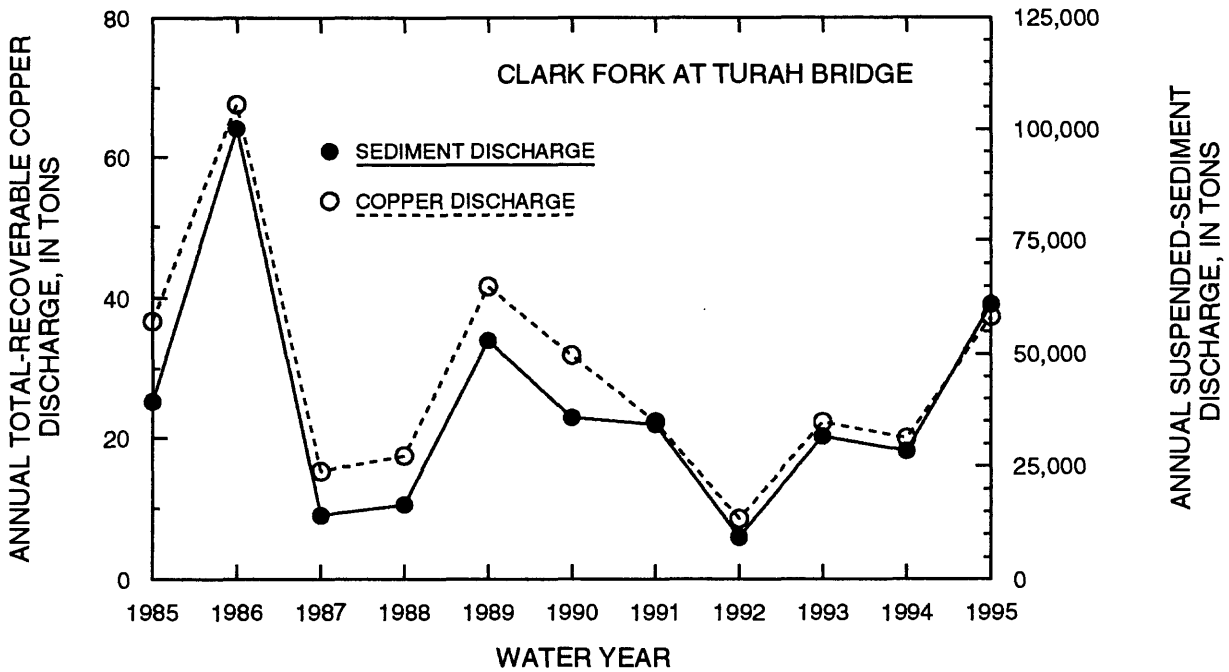


Figure 10. Annual suspended-sediment discharge and total-recoverable copper discharge for the Clark Fork at Turah Bridge, water years 1985-95.

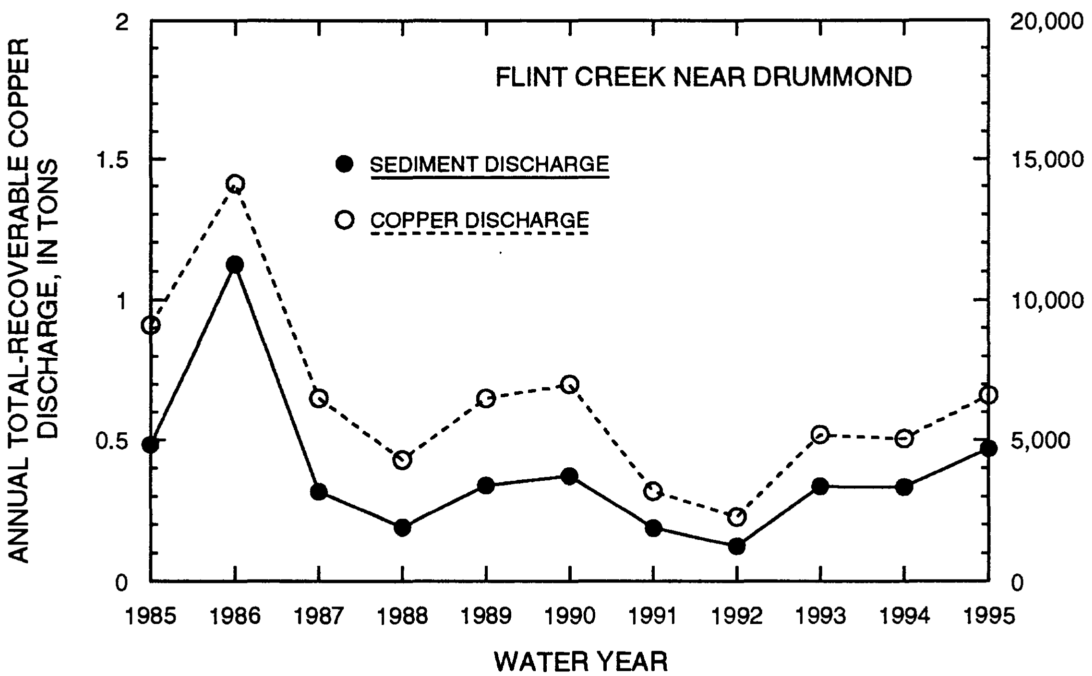


Figure 11. Annual suspended-sediment discharge and total-recoverable copper discharge for Flint Creek near Drummond, water years 1985-95.

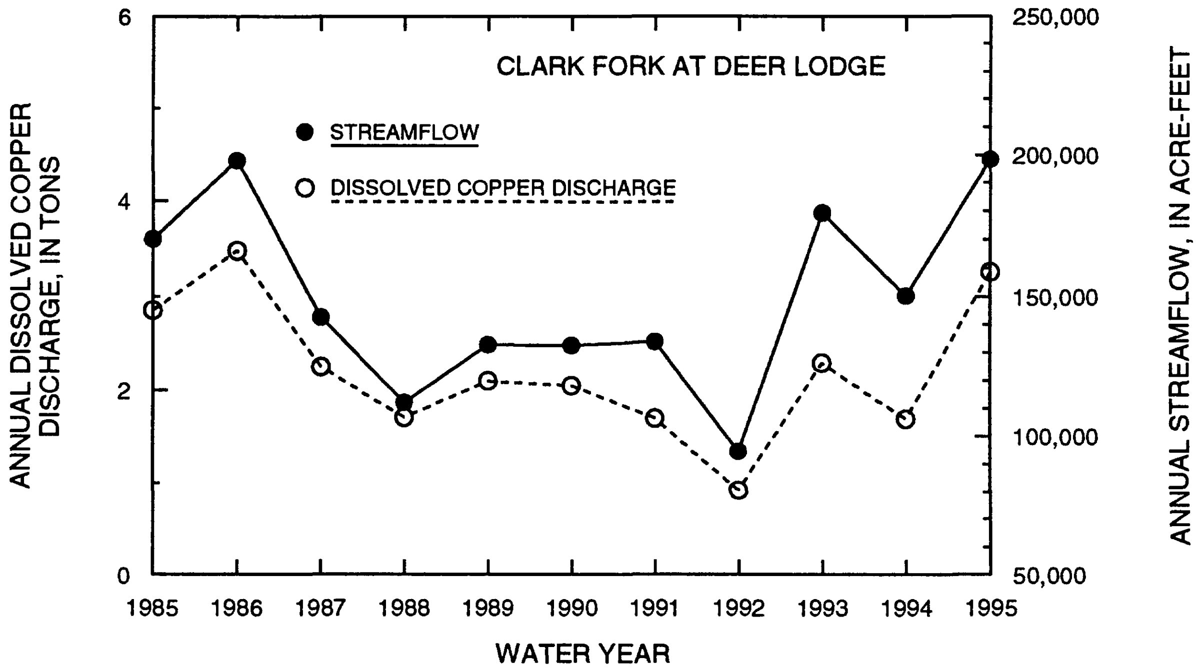


Figure 12. Annual streamflow and dissolved copper discharge for the Clark Fork at Deer Lodge, water years 1985-95.

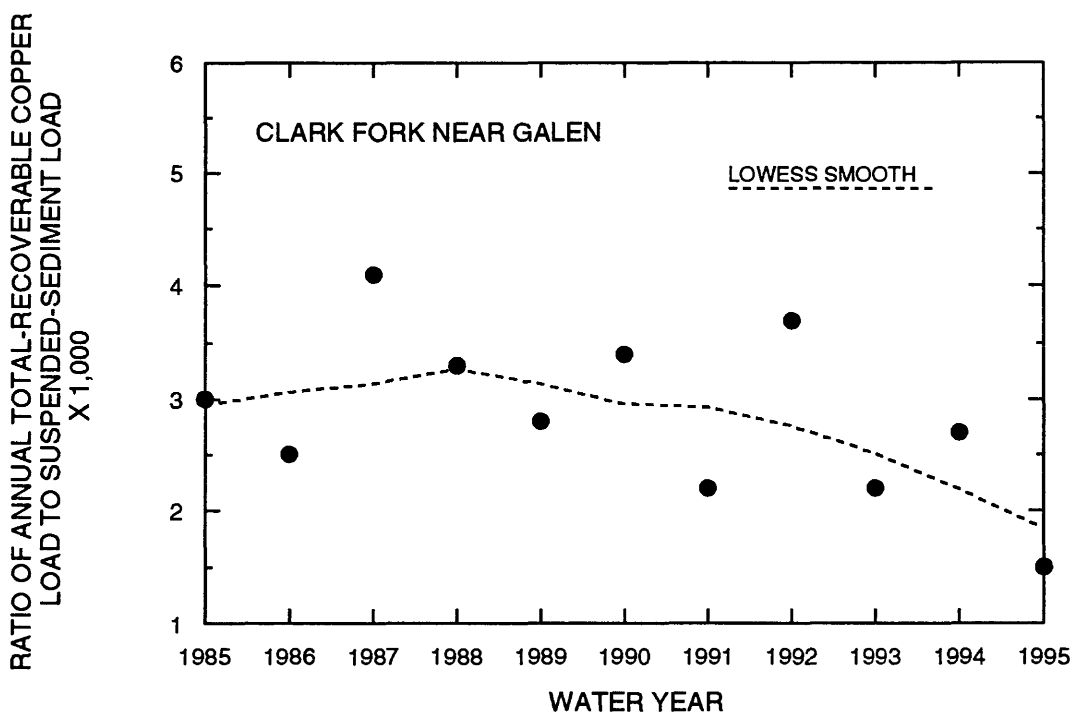


Figure 13. LOWESS-smooth temporal pattern for annual ratios of total-recoverable copper load to suspended-sediment load for the Clark Fork near Galen, water years 1985-95.

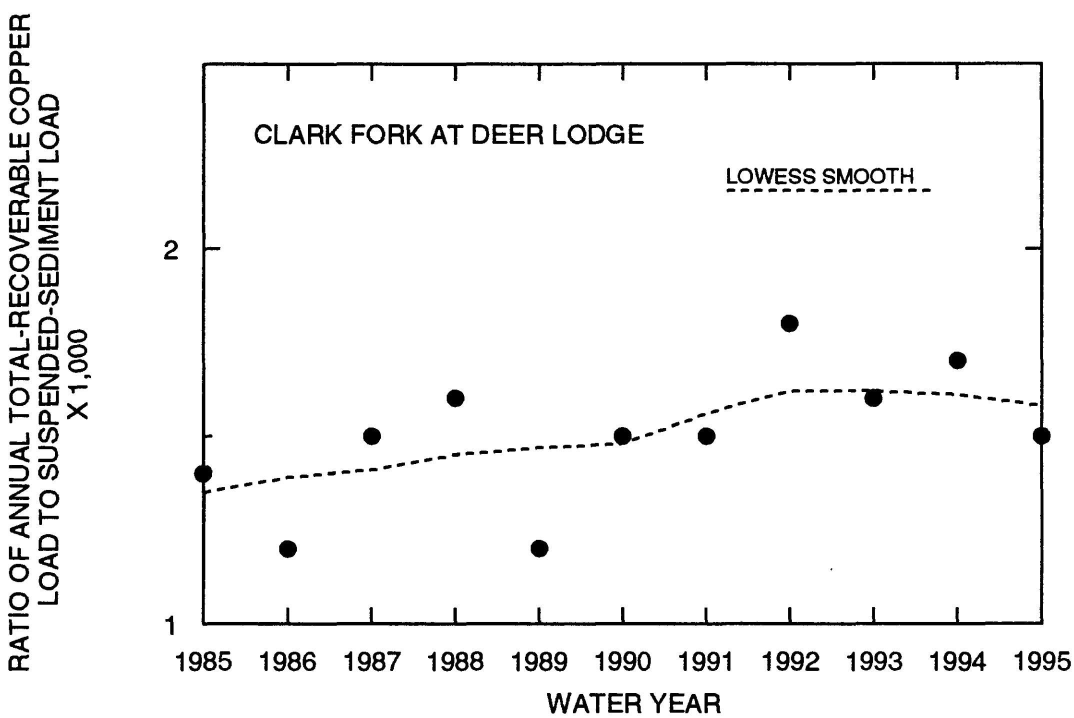


Figure 14. LOWESS-smooth temporal pattern for annual ratios of total-recoverable copper load to suspended-sediment load for the Clark Fork at Deer Lodge, water years 1985-95.

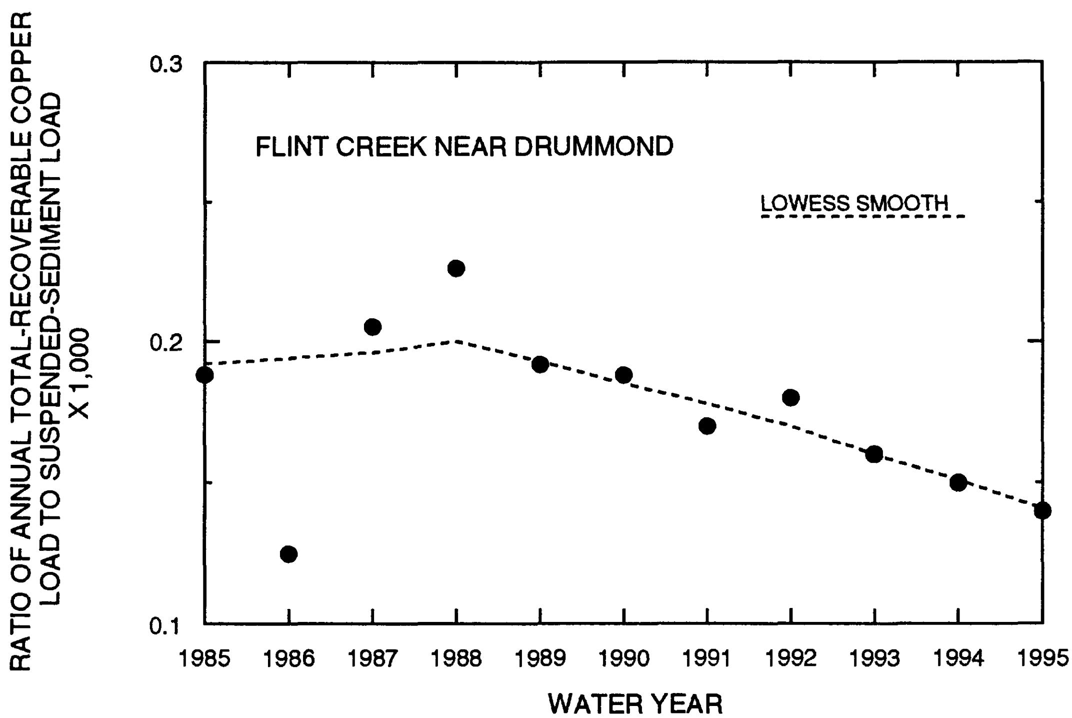


Figure 15. LOWESS-smooth temporal pattern for annual ratios of total-recoverable copper load to suspended-sediment load for Flint Creek near Drummond, water years 1985-95.

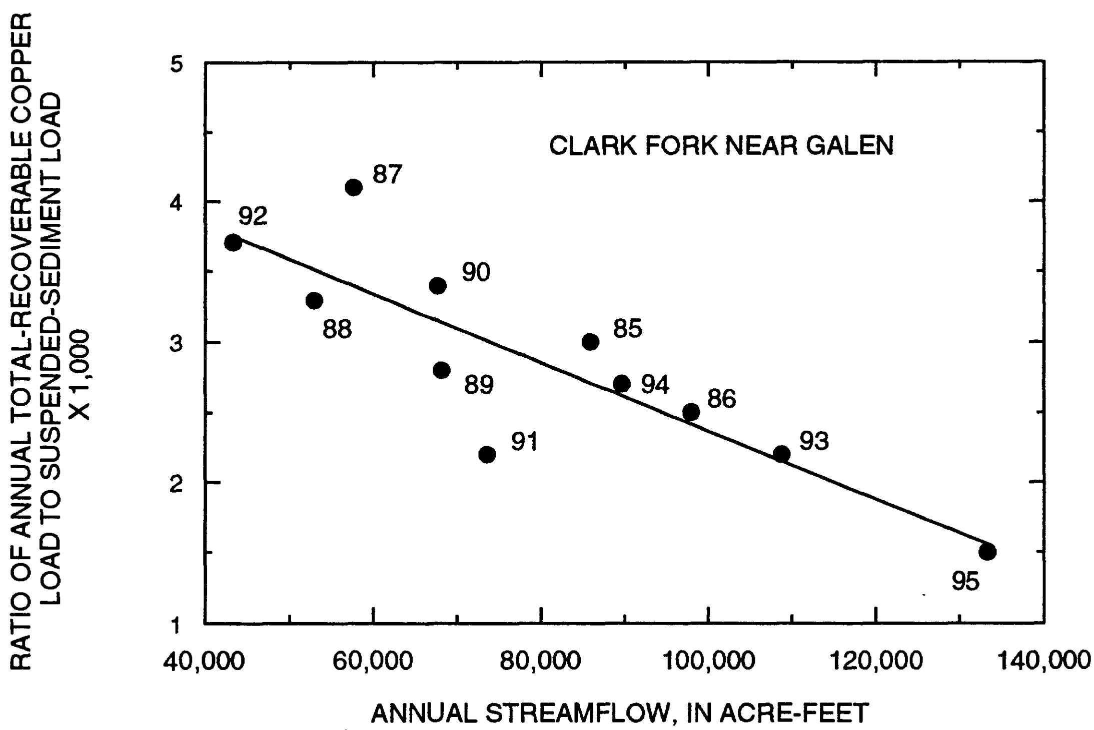


Figure 16. Relation of annual streamflow to annual ratios of total-recoverable copper load to suspended-sediment load for the Clark Fork near Galen, water years 1985-95.

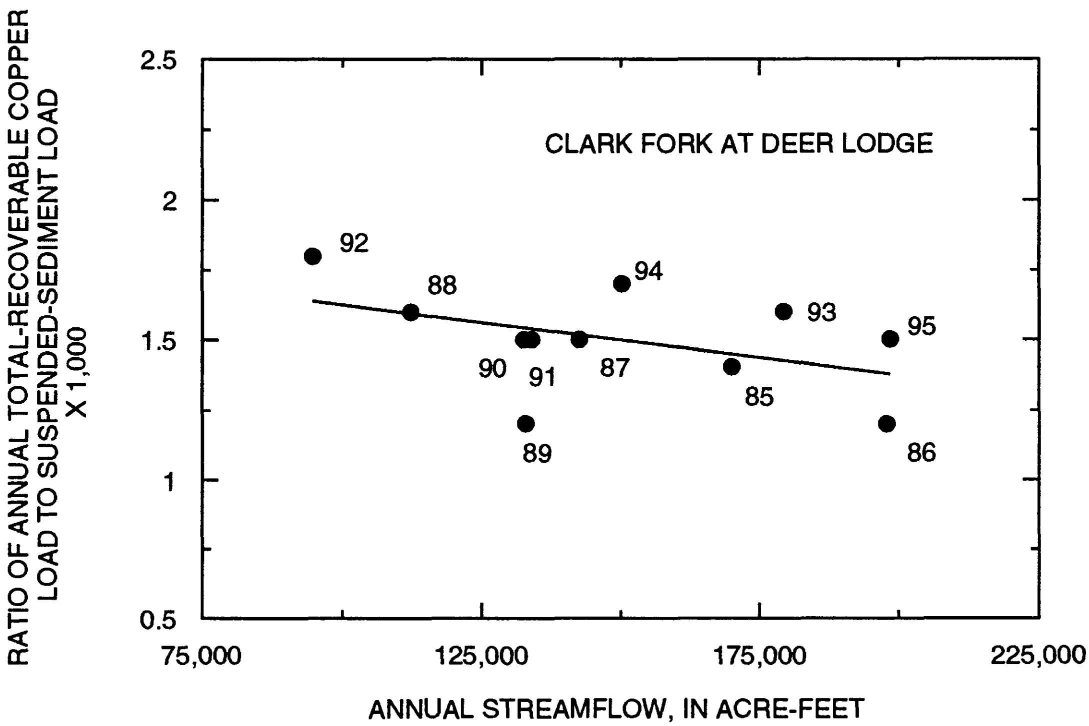


Figure 17. Relation of annual streamflow to annual ratios of total-recoverable copper load to suspended-sediment load for the Clark Fork at Deer Lodge, water years 1985-95.

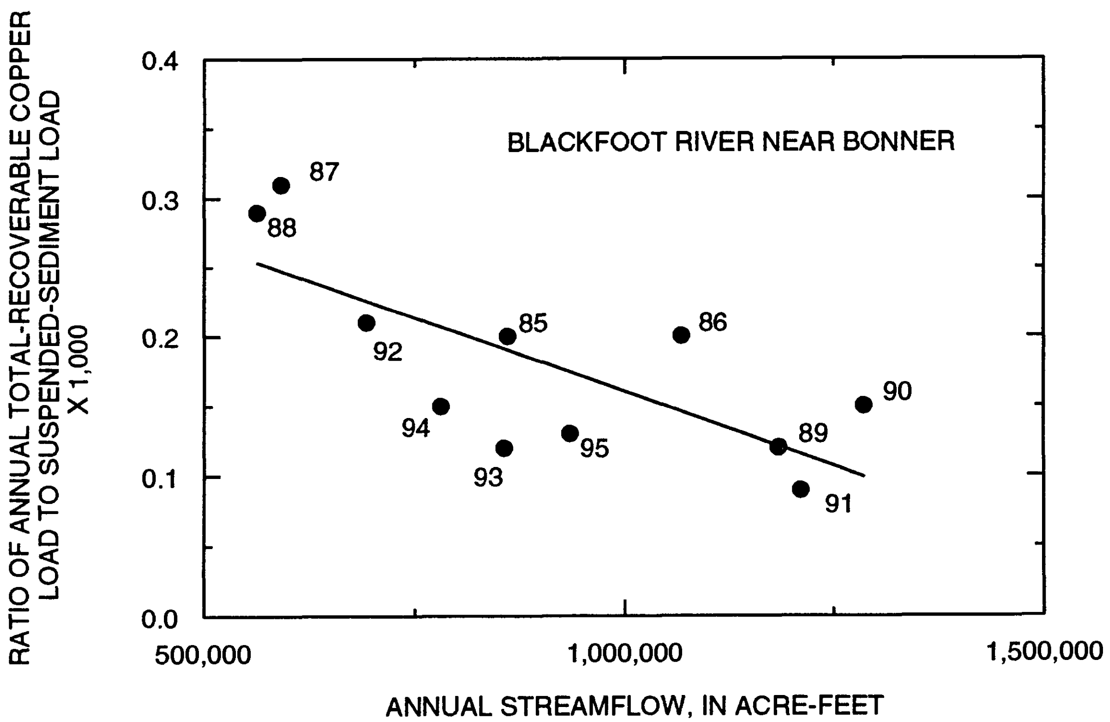


Figure 18. Relation of annual streamflow to annual ratios of total-recoverable copper load to suspended-sediment load for the Blackfoot River near Bonner, water years 1985-95.

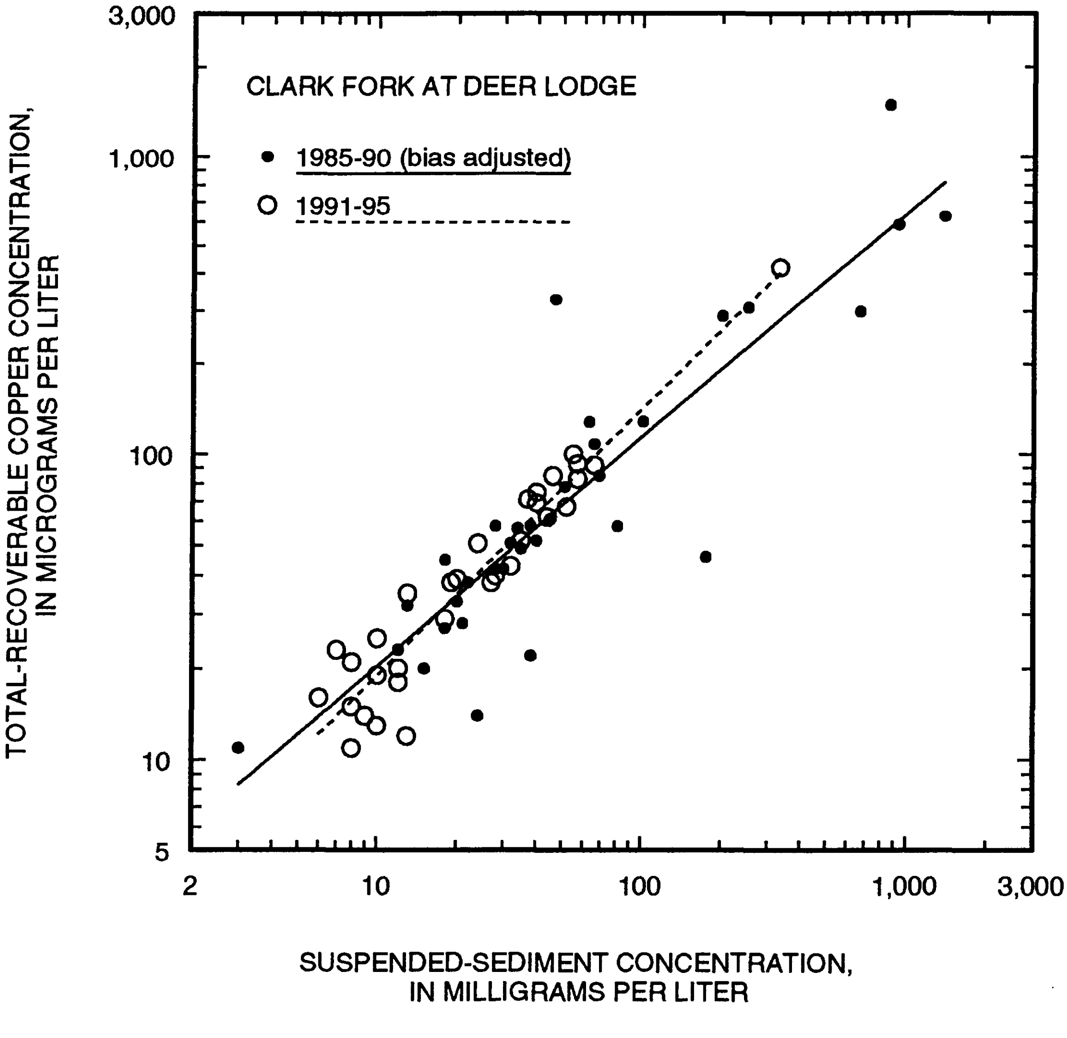


Figure 19. Relations of suspended-sediment concentration to total-recoverable copper concentration for water years 1985-90 and 1991-95.

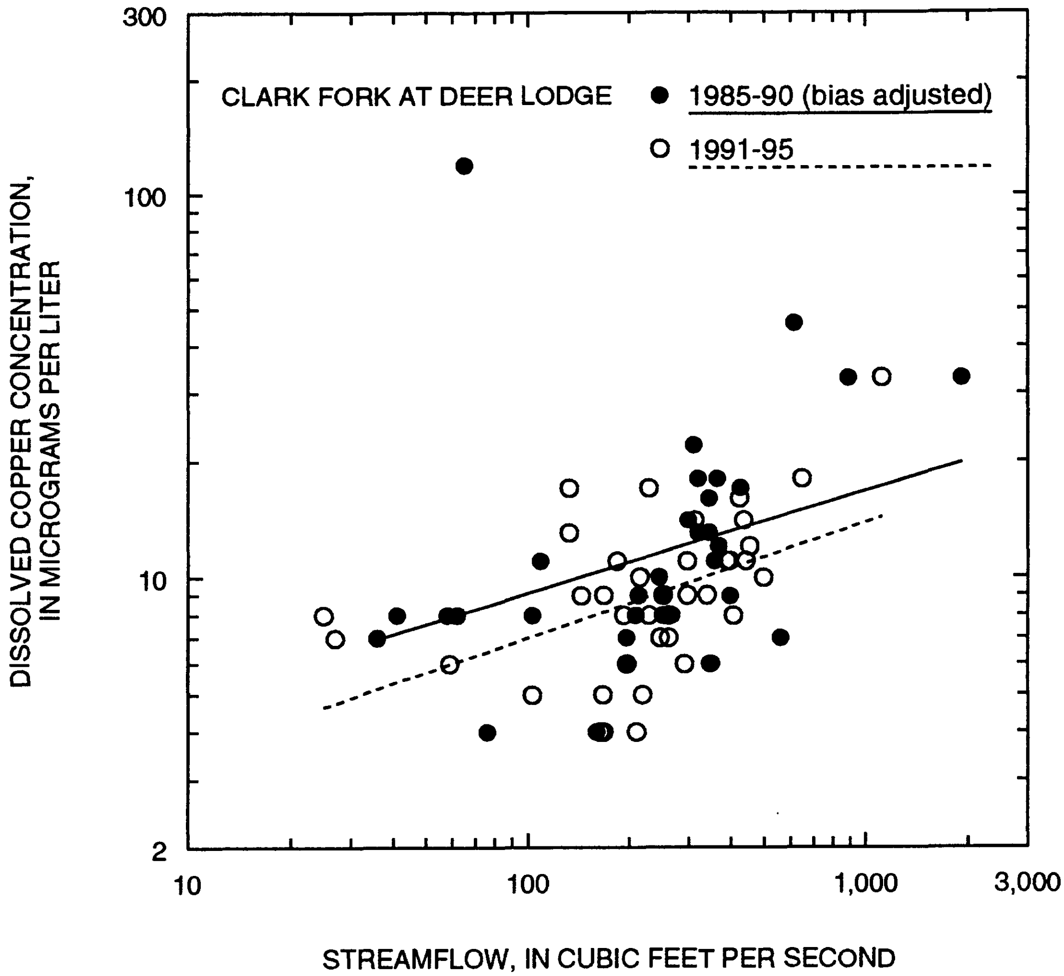
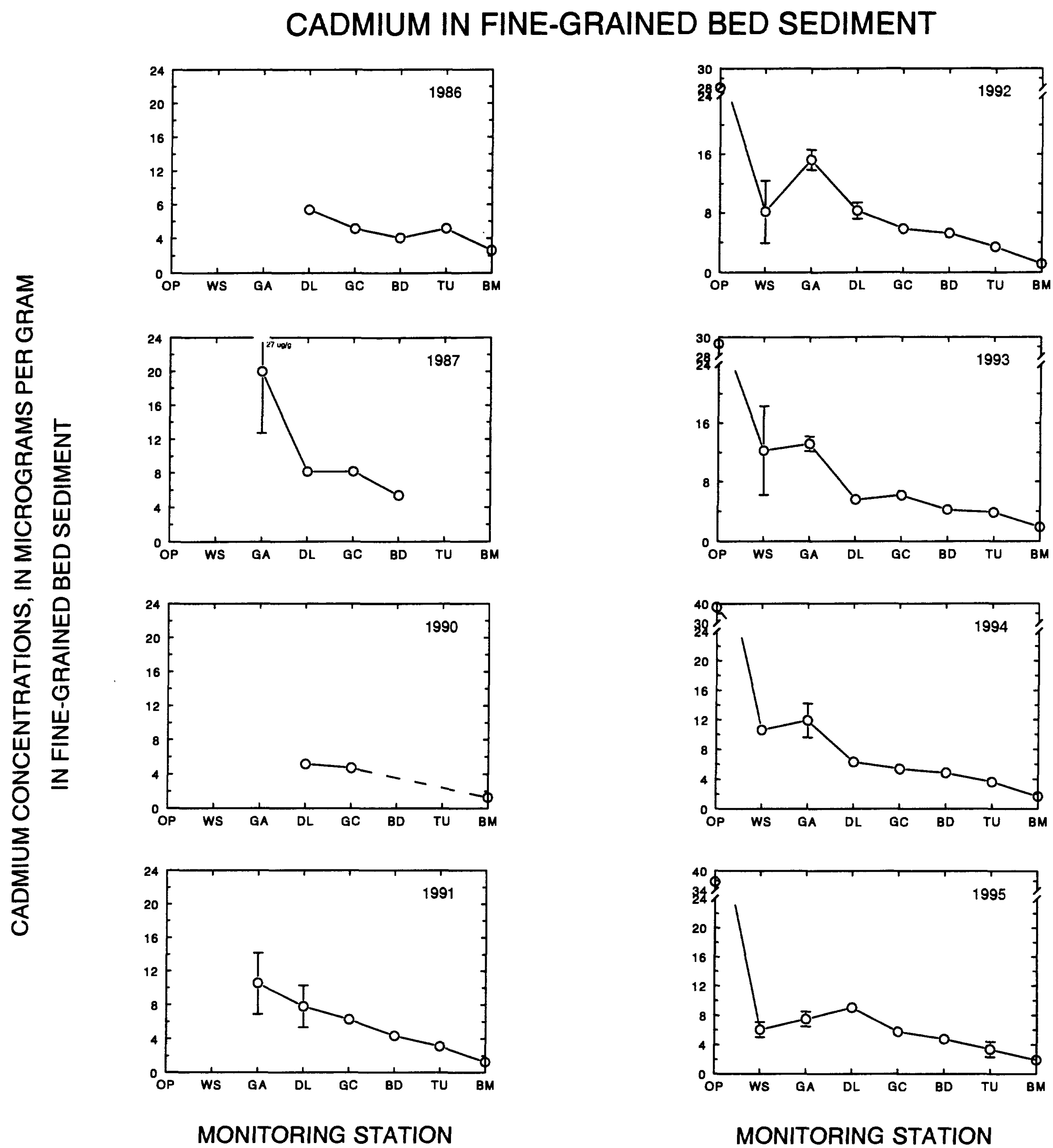
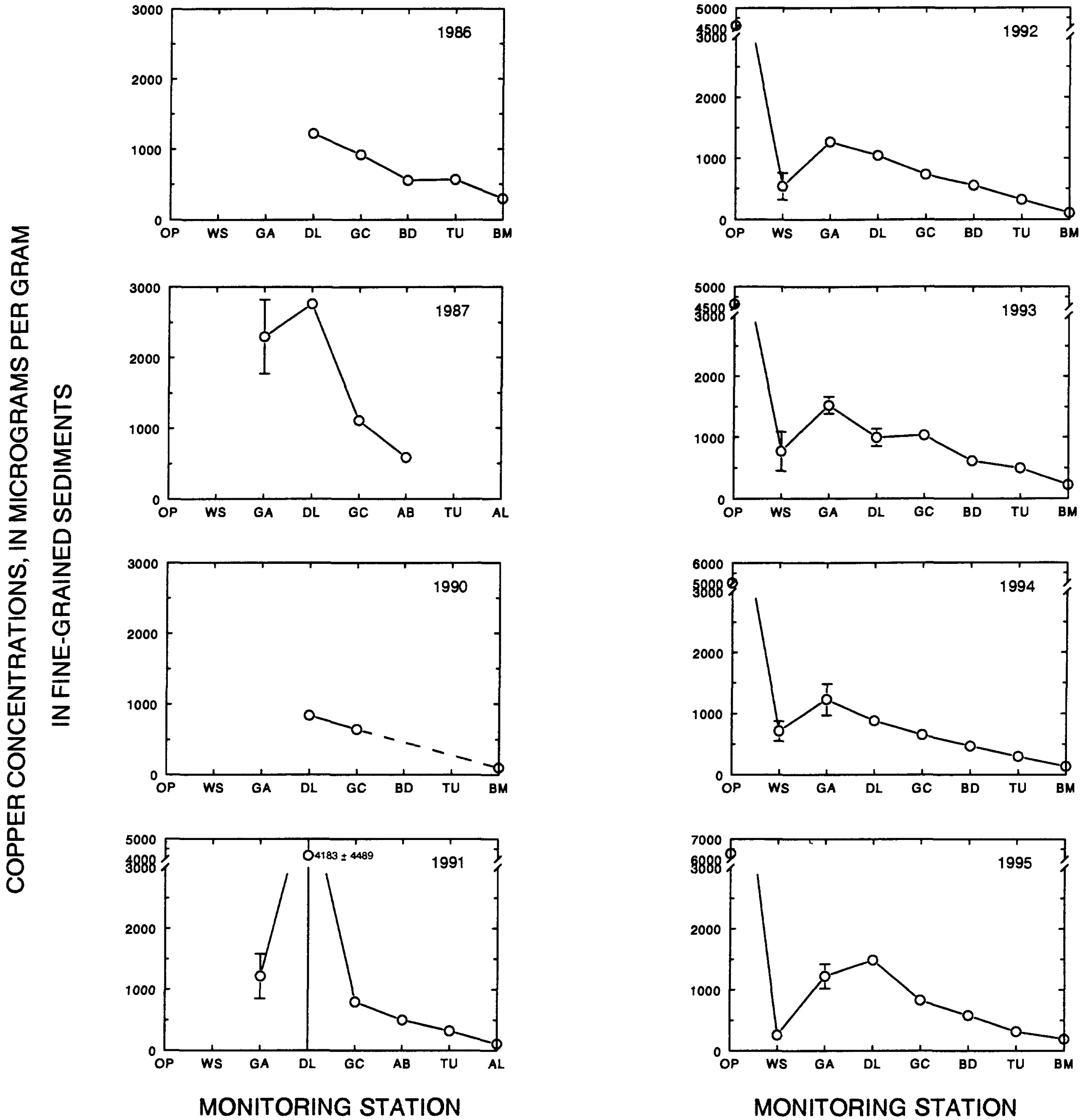


Figure 20. Relations of streamflow to dissolved copper concentration for water years 1985-90 and 1991-95.

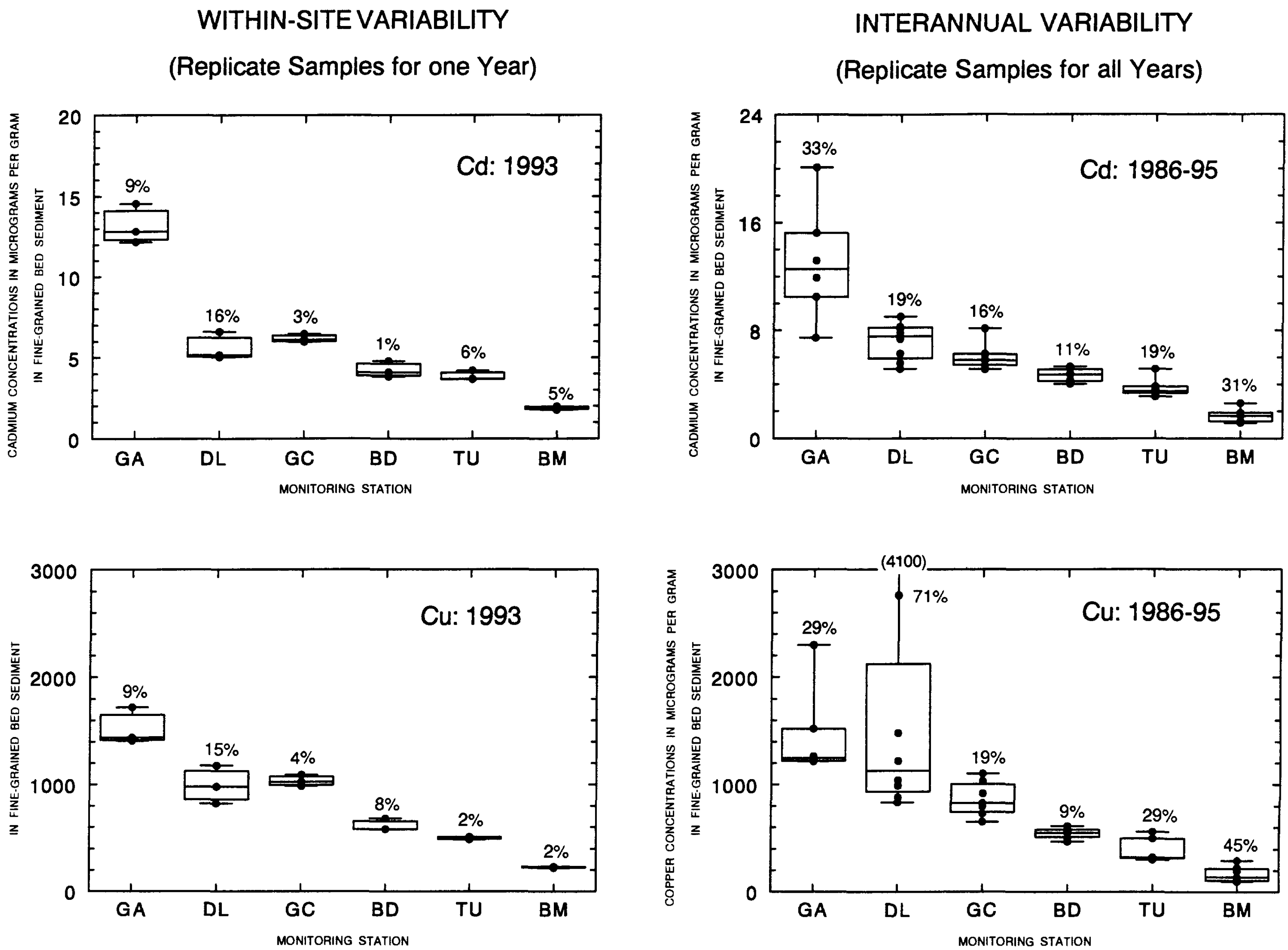


21. Downstream gradient of Cd concentrations in fine-grained bed sediment in the mainstem of the Clark Fork (1986-87; 1990-95). Station abbreviations: Silver Bow Creek at Opportunity (OP), Silver Bow Creek at Warm Springs (WS), Galen (GA), Deer Lodge (DL), Goldcreek (GC), below Drummond (BD), Turah (TU) and below Missoula (BM). Each symbol represents the mean concentration of three replicate samples. The vertical bar is the standard deviation of replicate sample values.

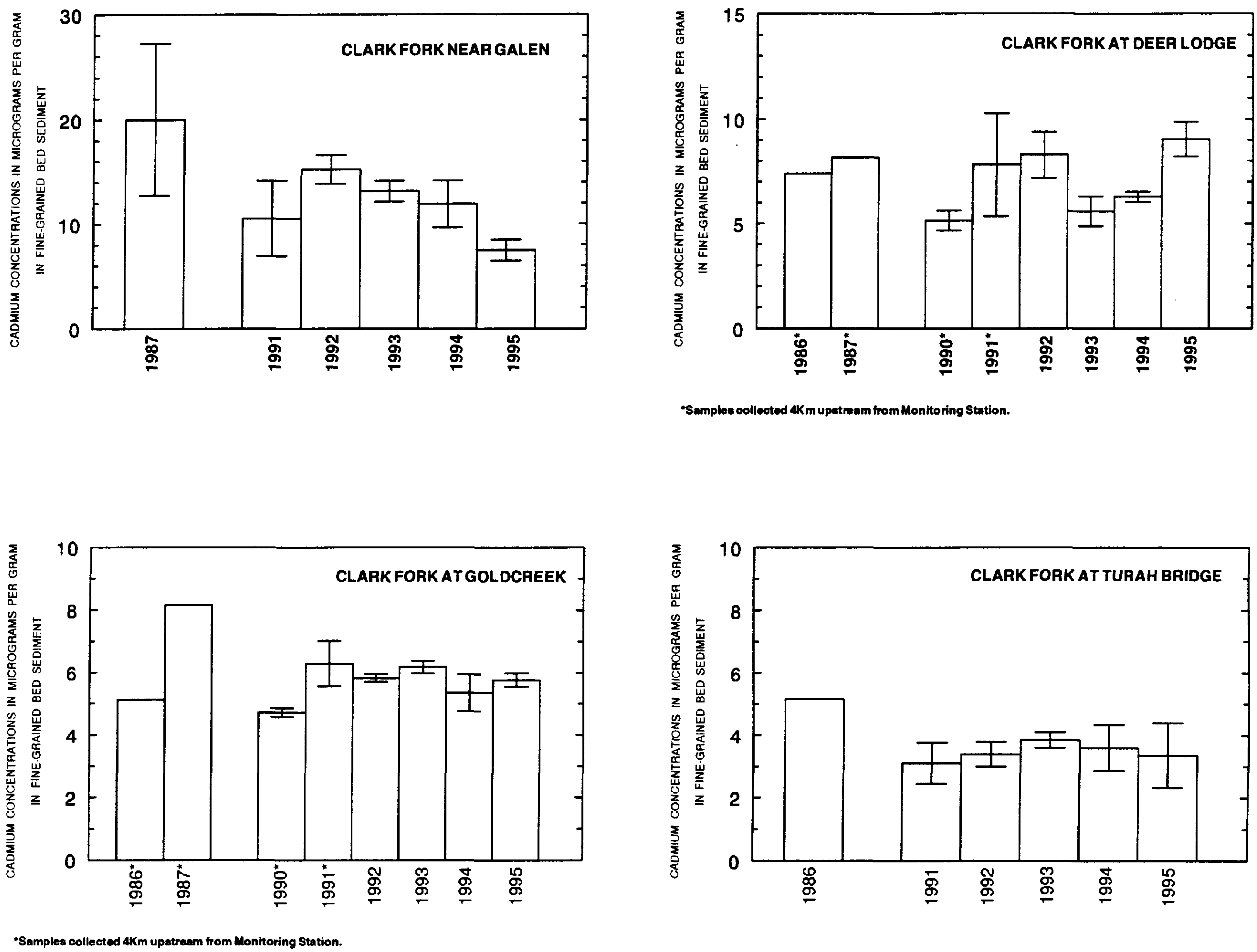
COPPER IN FINE-GRAINED BED SEDIMENT



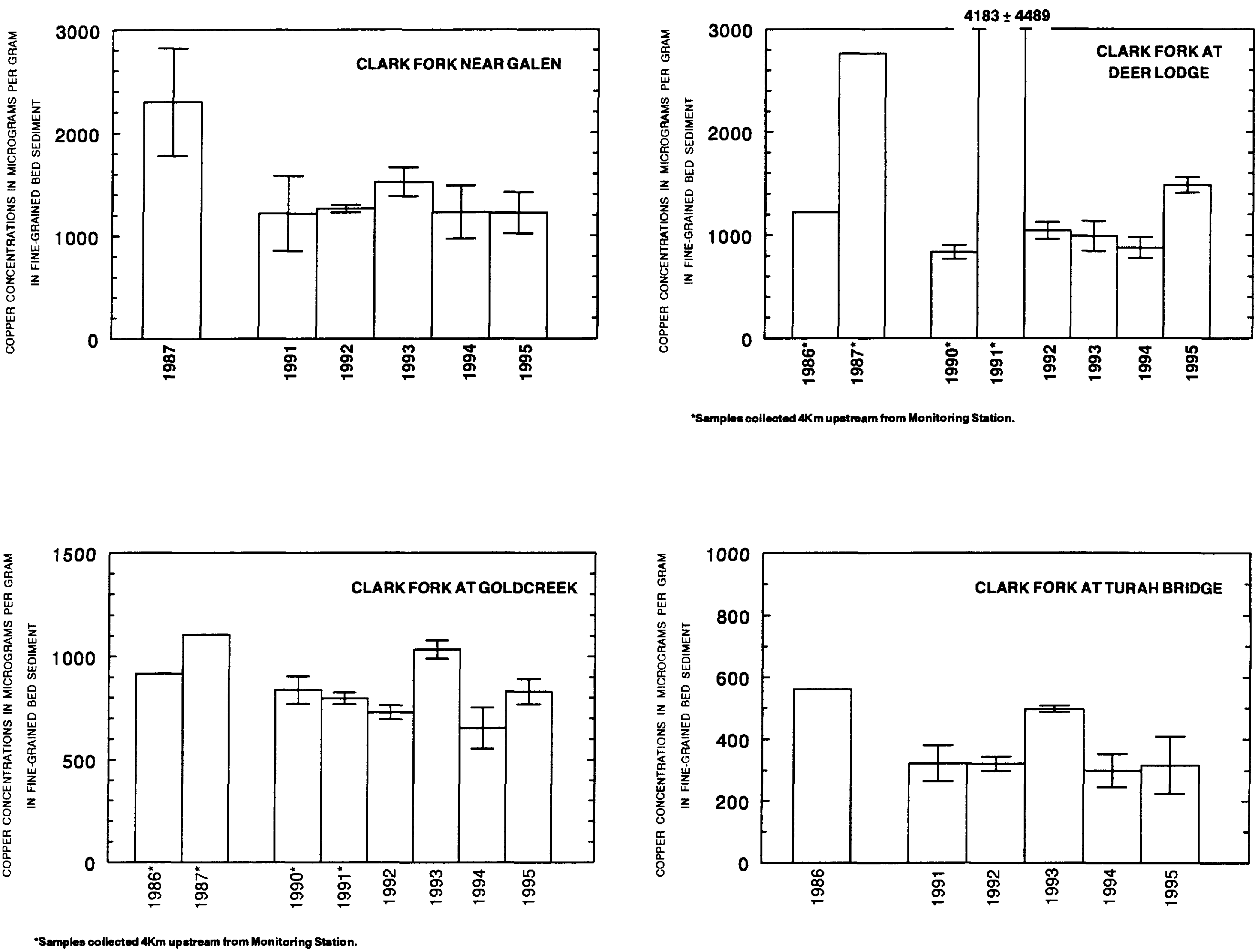
22. Downstream gradient of Cu concentrations in fine-grained bed sediment in the mainstem of the Clark Fork (1986-87; 1990-95). Station abbreviations: Silver Bow Creek at Opportunity (OP), Silver Bow Creek at Warm Springs (WS), Galen (GA), Deer Lodge (DL), Goldcreek (GC), below Drummond (BD), Turah (TU) and below Missoula (BM). Each symbol represents the mean concentration of three replicate samples. The vertical bar is the standard deviation of replicate sample values.



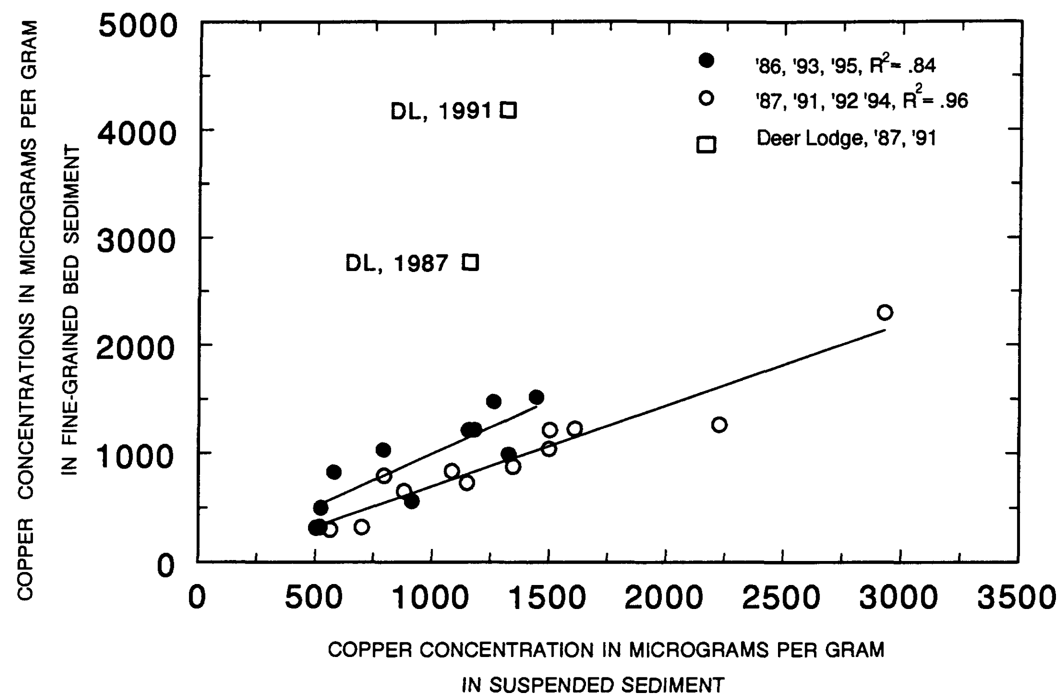
23. Within-site and interannual variability of Cd and Cu concentrations in fine-grained bed sediment at Galen (GA), Deer Lodge (DL), Goldcreek (GC), below Drummond (BD), Turah (TU) and below Missoula (BM). The box shows the range between the 25th and 75th percentiles, the horizontal line represents the median value, and the whiskers extend to the 5th and the 95th percentiles of the data. Values listed above each plot show the coefficient of variation (CV), expressed as a percent.



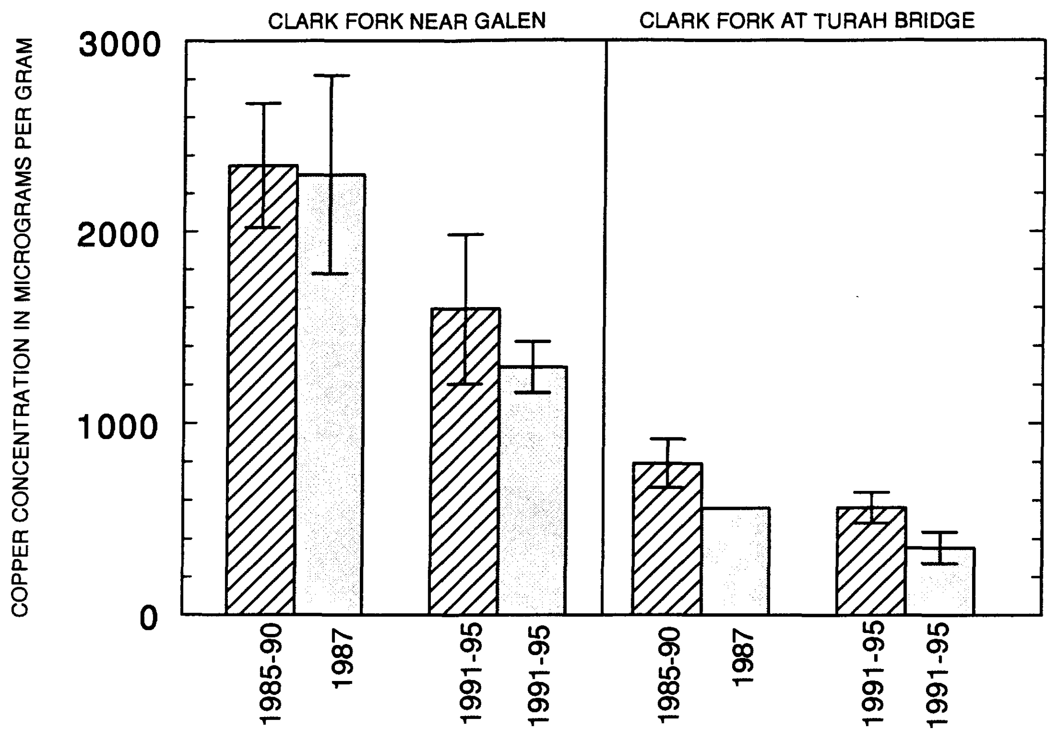
24. Annual mean concentrations of Cd in fine-grained bed sediment at four Clark Fork mainstem stations. The vertical bar is the standard deviation of replicate sample values.



25. Annual mean concentrations of Cu in fine-grained bed sediment at four Clark Fork mainstem stations. The vertical bar is the standard deviation of replicate sample values.

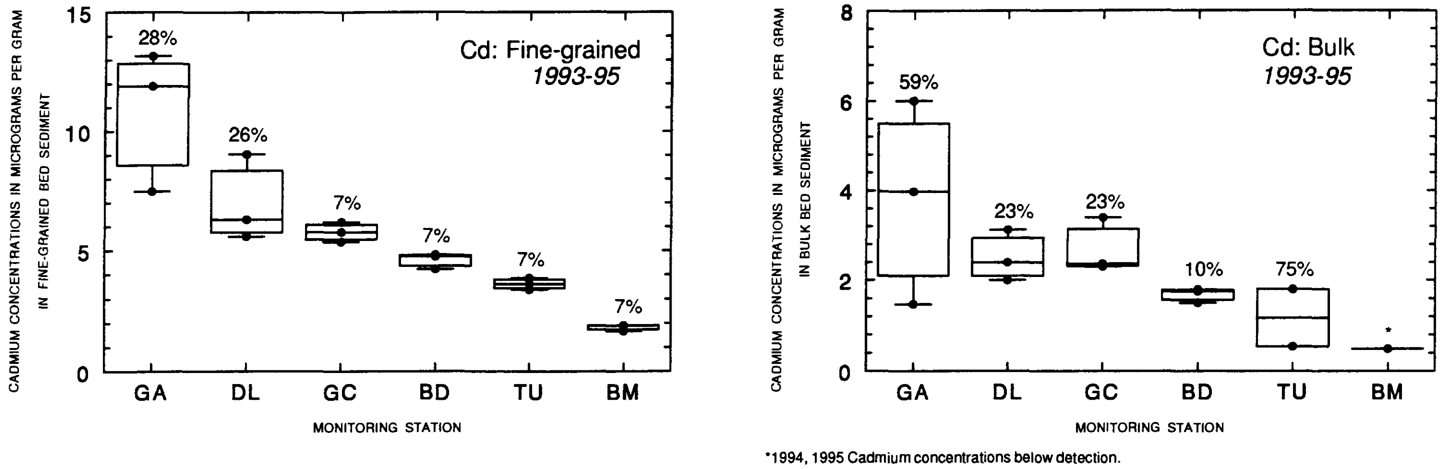


26. Relation of estimated annual mean Cu concentrations in suspended sediment to annual mean Cu concentrations in fine-grained bed sediment at four mainstem stations (Galen, Deer Lodge, Goldcreek and Turah). Solid circles are Cu concentrations in high flow years; open circles are Cu concentrations in low flow years. Squares are concentrations at the Deer Lodge station in 1987 and 1991.

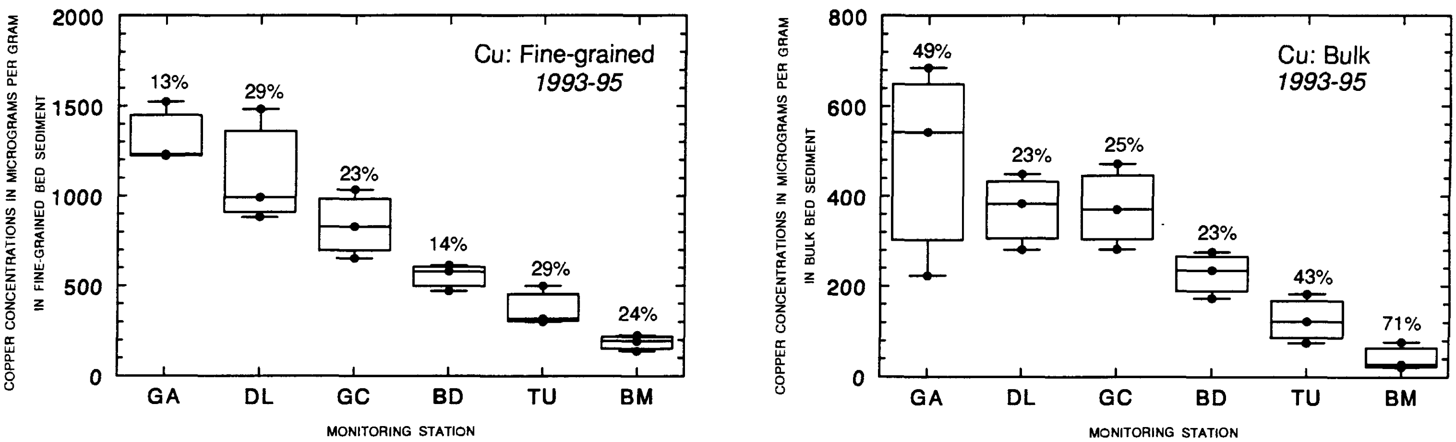


27. Estimated mean Cu concentrations in suspended sediment (hatched bar) and mean Cu concentrations in fine-grained bed sediment (solid bar) at two monitoring sites for the 1985-1990 and 1991-1995 periods. The vertical bar is the standard deviation of replicate sample values.

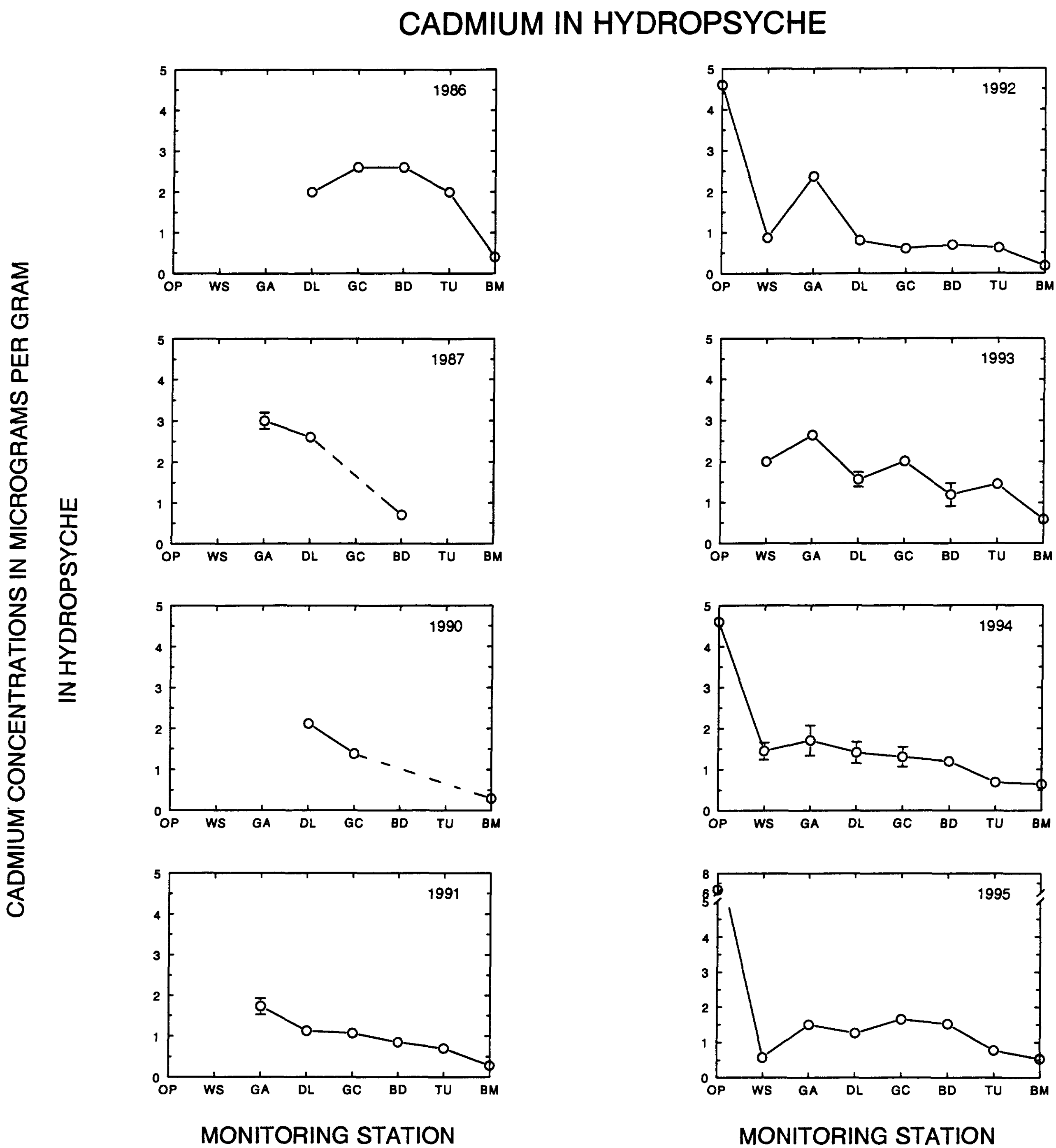
CADMIUM



COPPER

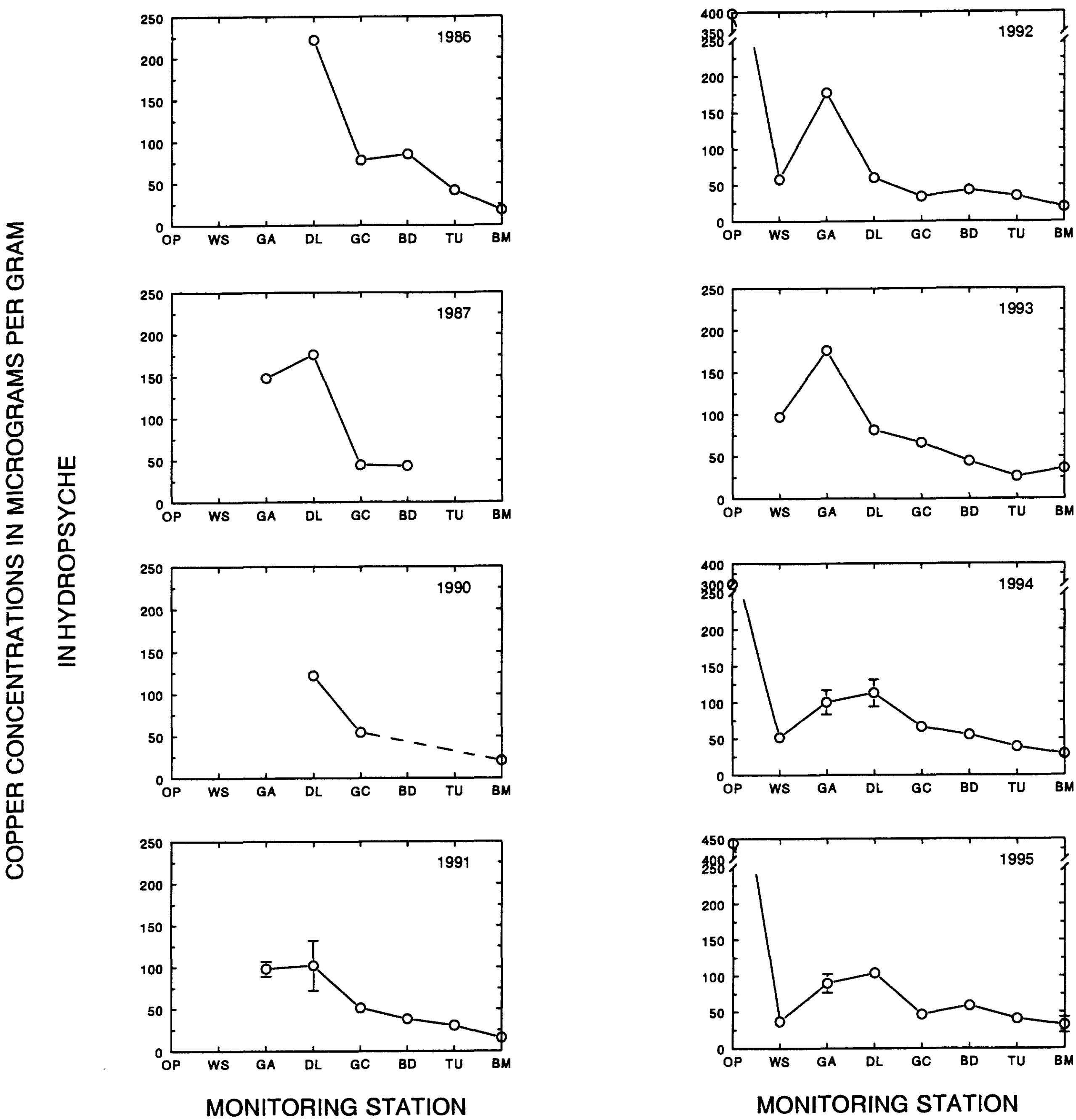


28. Box plots of Cd and Cu concentrations in fine-grained and bulk bed sediment at Galen (GA), Deer Lodge (DL), Goldcreek (GC), below Drummond (BD), Turah (TU), and below Missoula (BM). The box shows the range between the 25th and 75th percentiles, the horizontal line represents the median value, and the whiskers extend to the 5th and the 95th percentiles of the data. Values listed above each plot show the coefficient of variation (CV), expressed as a percent.

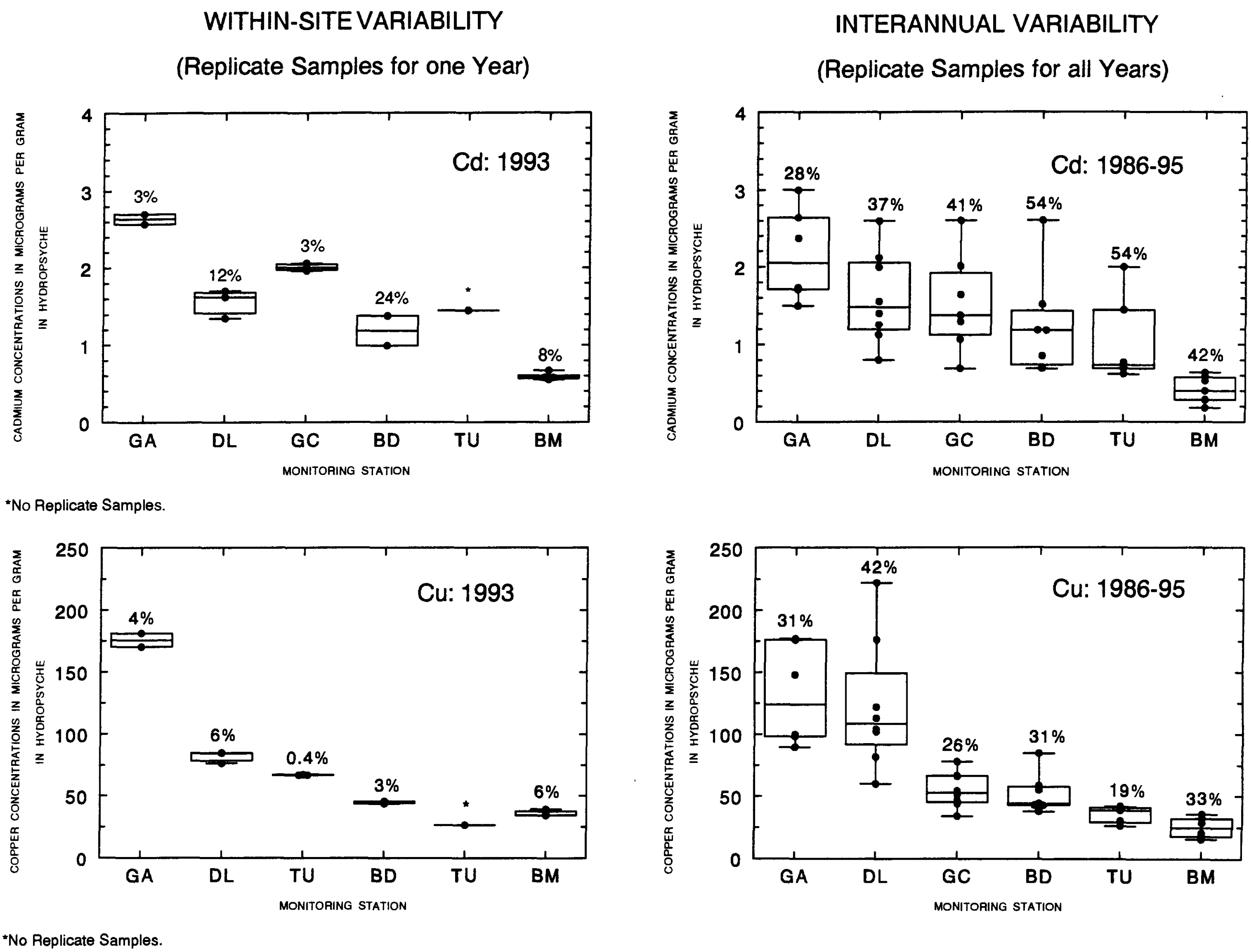


29. Downstream gradient of Cd concentrations in the caddisfly *Hydropsyche* in the mainstem of the Clark Fork (1986-87; 1990-95). Station abbreviations: Silver Bow Creek at Opportunity (OP), Silver Bow Creek at Warm Springs (WS), Galen (GA), Deer Lodge (DL), Goldcreek (GC), below Drummond (BD), Turah (TU) and below Missoula (BM). The vertical bar is the standard deviation of replicate sample values.

COPPER IN HYDROPSYCHE

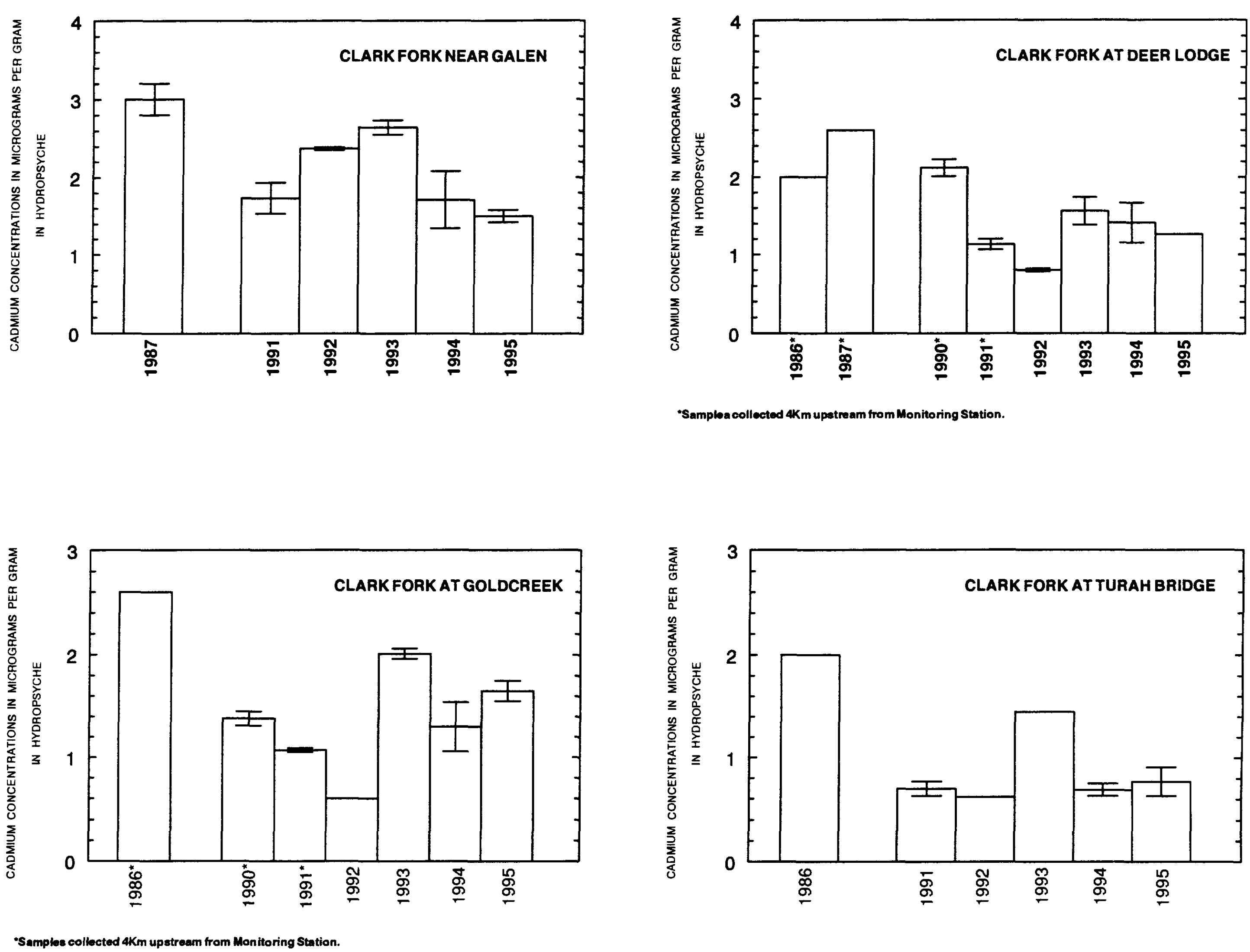


30. Downstream gradient of Cu concentrations in the caddisfly *Hydropsyche* in the mainstem of the Clark Fork (1986-87; 1990-95). Station abbreviations: Silver Bow Creek at Opportunity (OP), Silver Bow Creek at Warm Springs (WS), Galen (GA), Deer Lodge (DL), Goldcreek (GC), below Drummond (BD), Turah (TU) and below Missoula (BM). The vertical bar is the standard deviation of replicate sample values.



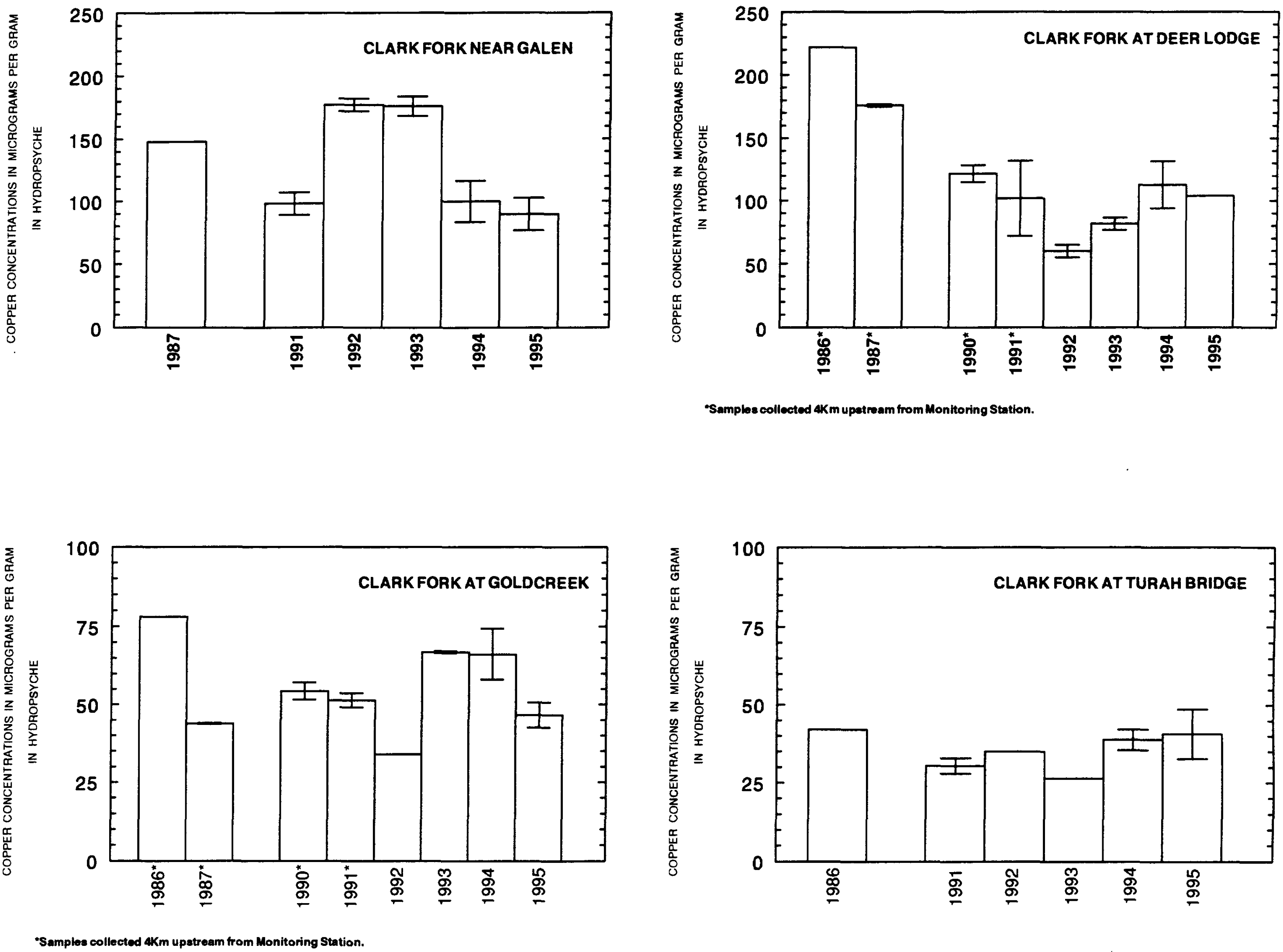
31. Within-site and interannual variability of Cd and Cu concentrations in *Hydropsyche* at Galen (GA), Deer Lodge (DL), Goldcreek (GC), below Drummond (BD), Turah (TU) and below Missoula (BM). The box shows the range between the 25th and 75th percentiles, the horizontal line represents the median value, and the whiskers extend to the 5th and the 95th percentiles, of the data. Values listed above each plot show the coefficient of variation (CV), expressed as a percent.

CADMIUM



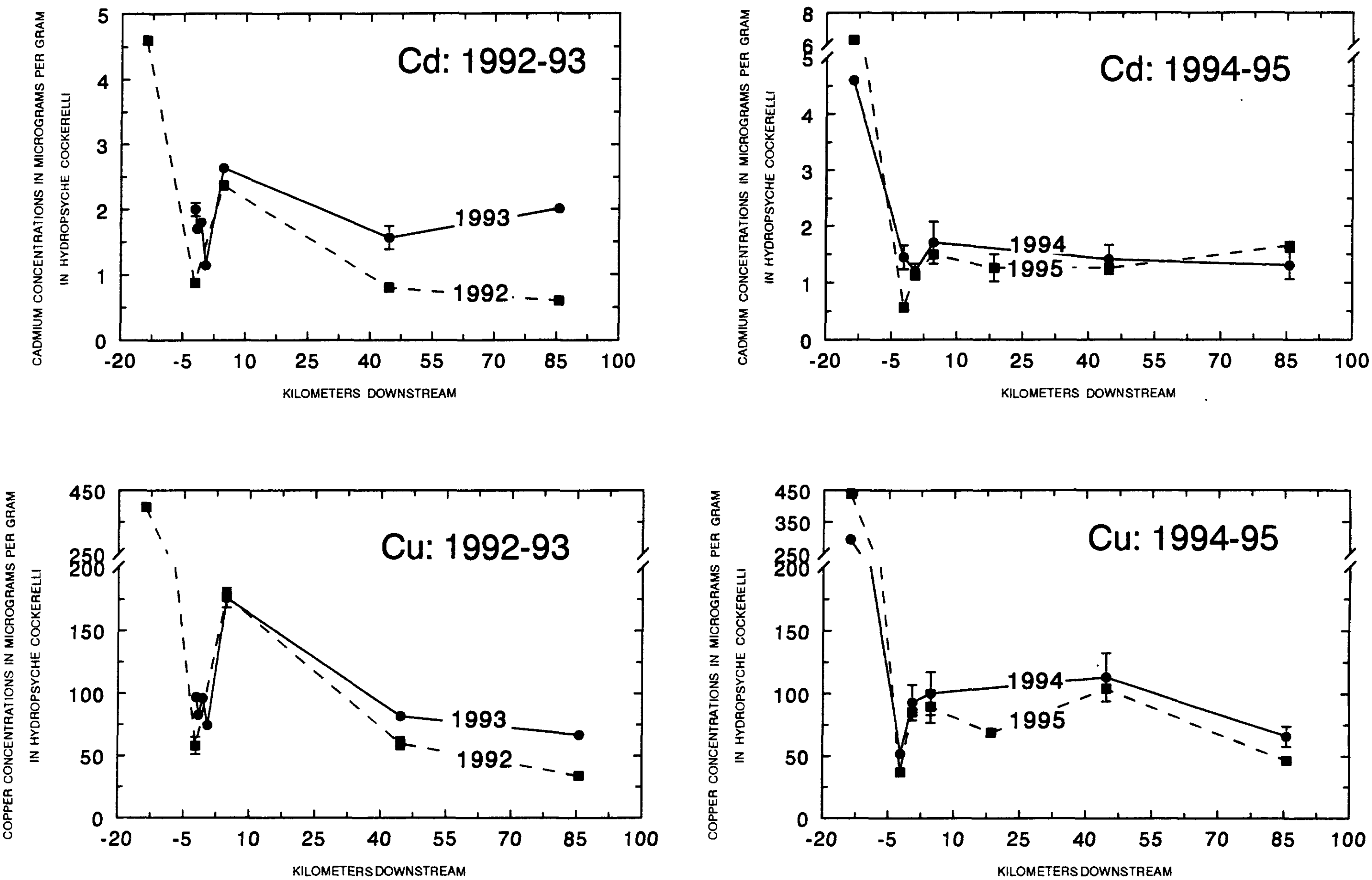
32. Annual mean concentrations of Cd in *Hydropsyche* at four Clark Fork mainstem stations. The vertical bar is the standard deviation of replicate sample values.

COPPER



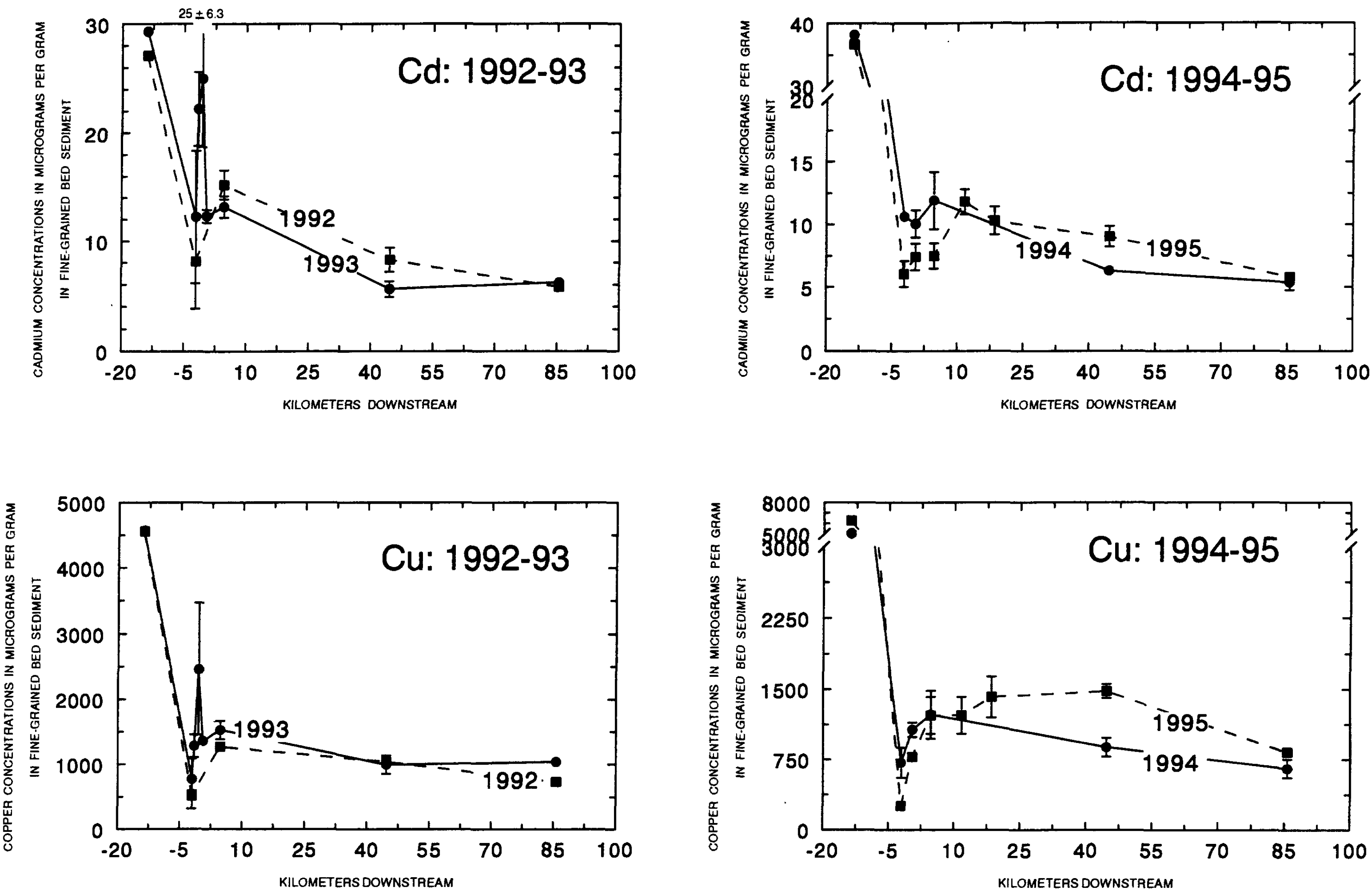
33. Annual mean concentrations of Cu in *Hydropsyche* at four Clark Fork mainstem stations. The vertical bar is the standard deviation of replicate sample values.

HYDROPSYCHE



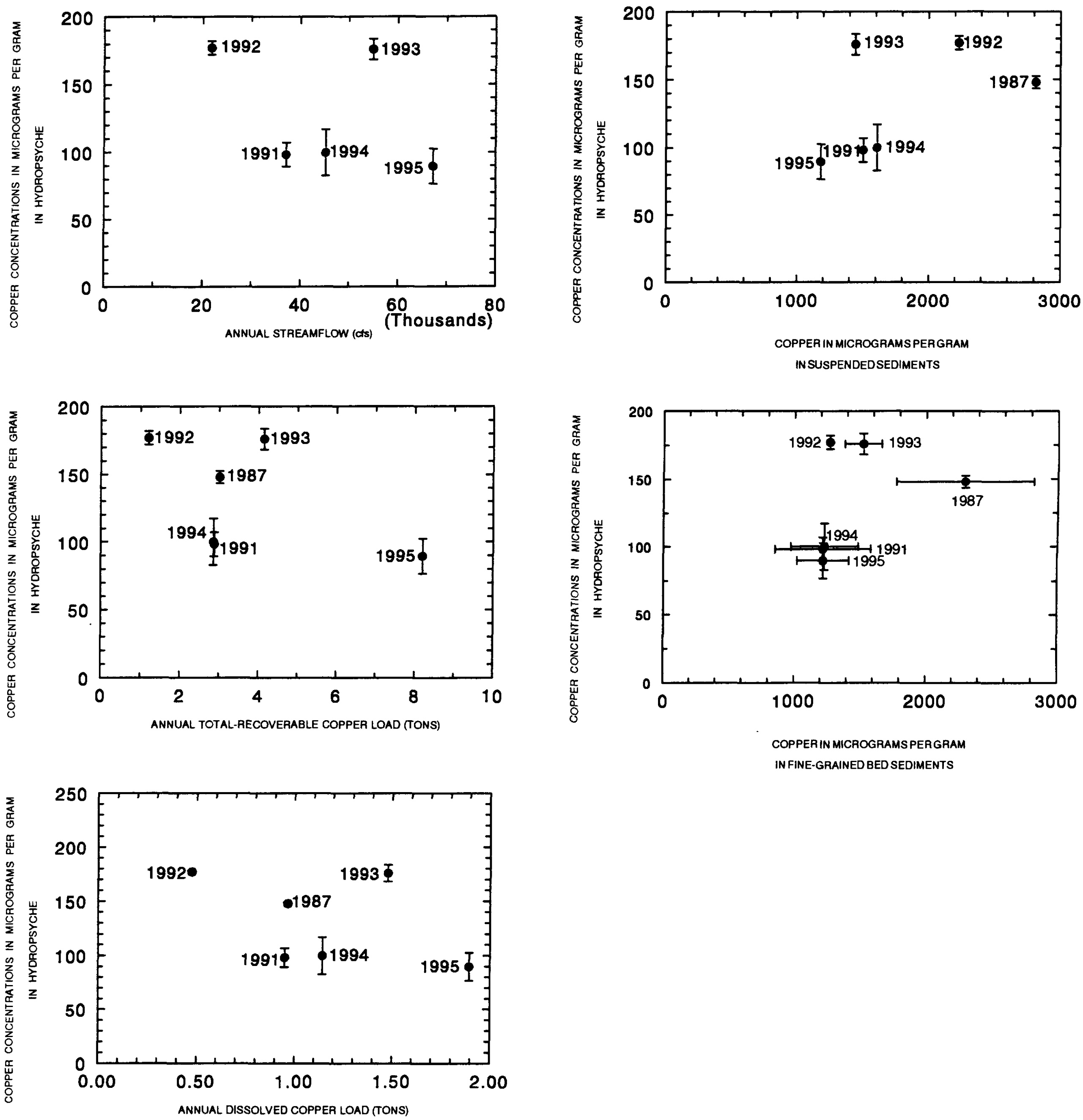
34. Detailed spatial distribution of Cd and Cu concentrations in *Hydropsyche* in the most upstream segment of the Clark Fork (1992-1995). The vertical bar is the standard deviation of replicate sample values.

FINE-GRAINED BED SEDIMENT



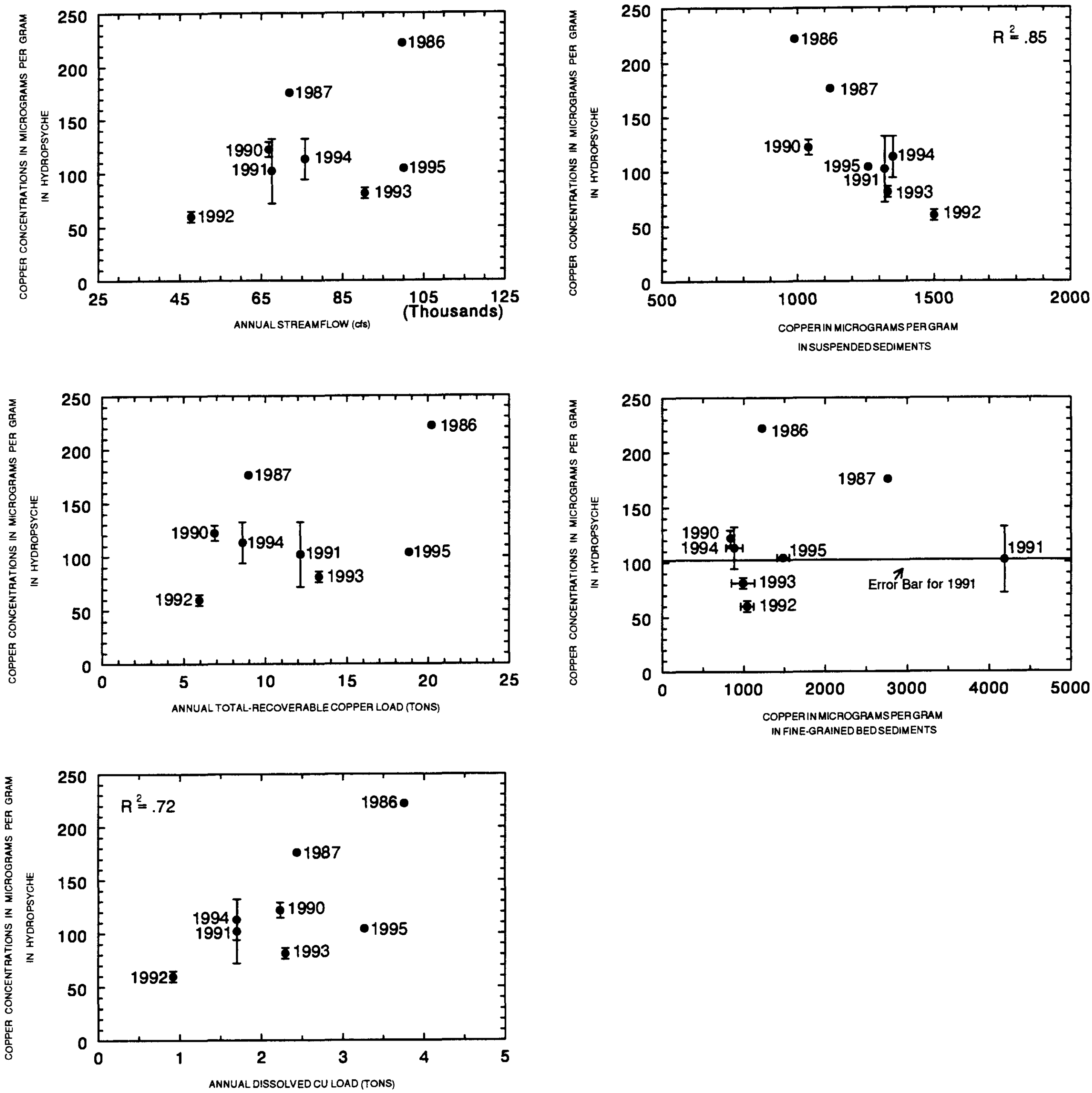
35. Detailed spatial distribution of Cd and Cu concentrations in fine-grained bed sediment in the most upstream segment of the Clark Fork (1992-1995). The vertical bar is the standard deviation of replicate sample values.

GALEN



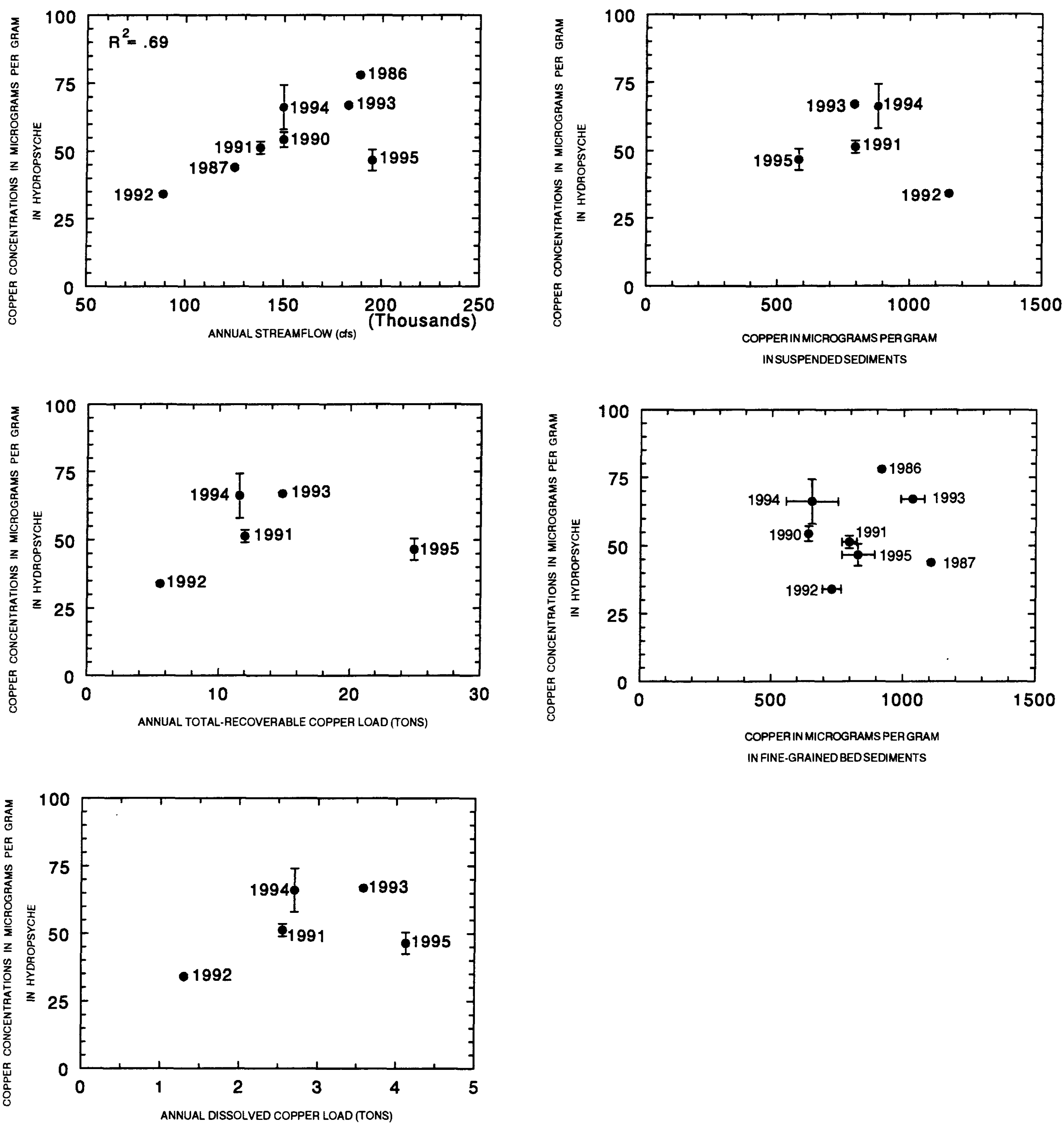
36. Relation between annual Cu concentrations in *Hydropsyche* and total annual streamflow, annual total-recoverable Cu load, annual dissolved Cu load, estimated annual Cu concentrations in suspended sediment, and Cu concentration in fine-grained bed sediment at Galen. The vertical bar is the standard deviation of replicate sample values.

DEER LODGE

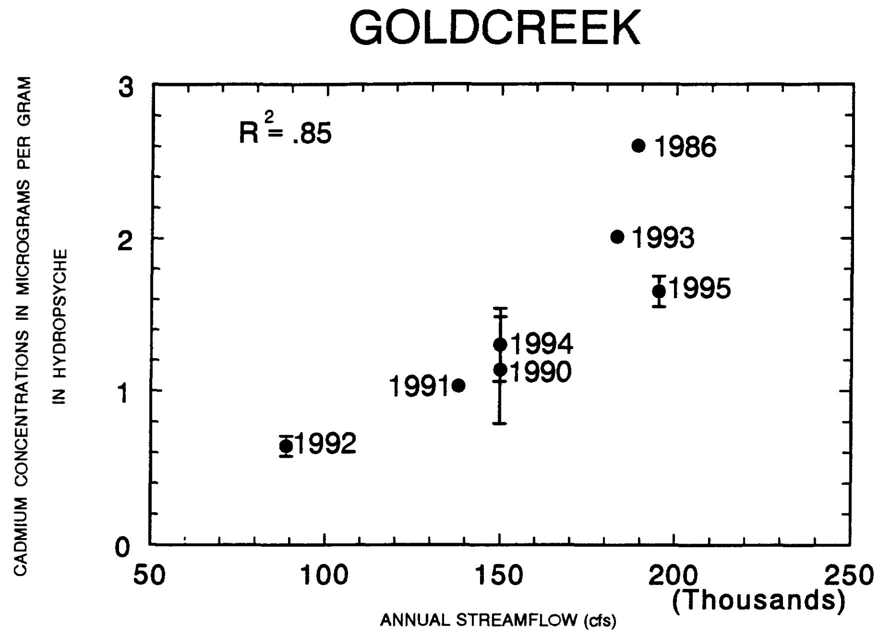


37. Relation between annual Cu concentrations in *Hydropsyche* and total annual streamflow, annual total-recoverable Cu load, annual dissolved Cu load, estimated annual Cu concentrations in suspended sediment, and Cu concentration in fine-grained bed sediment at Deer Lodge. The vertical bar is the standard deviation of replicate sample values.

GOLDCREEK

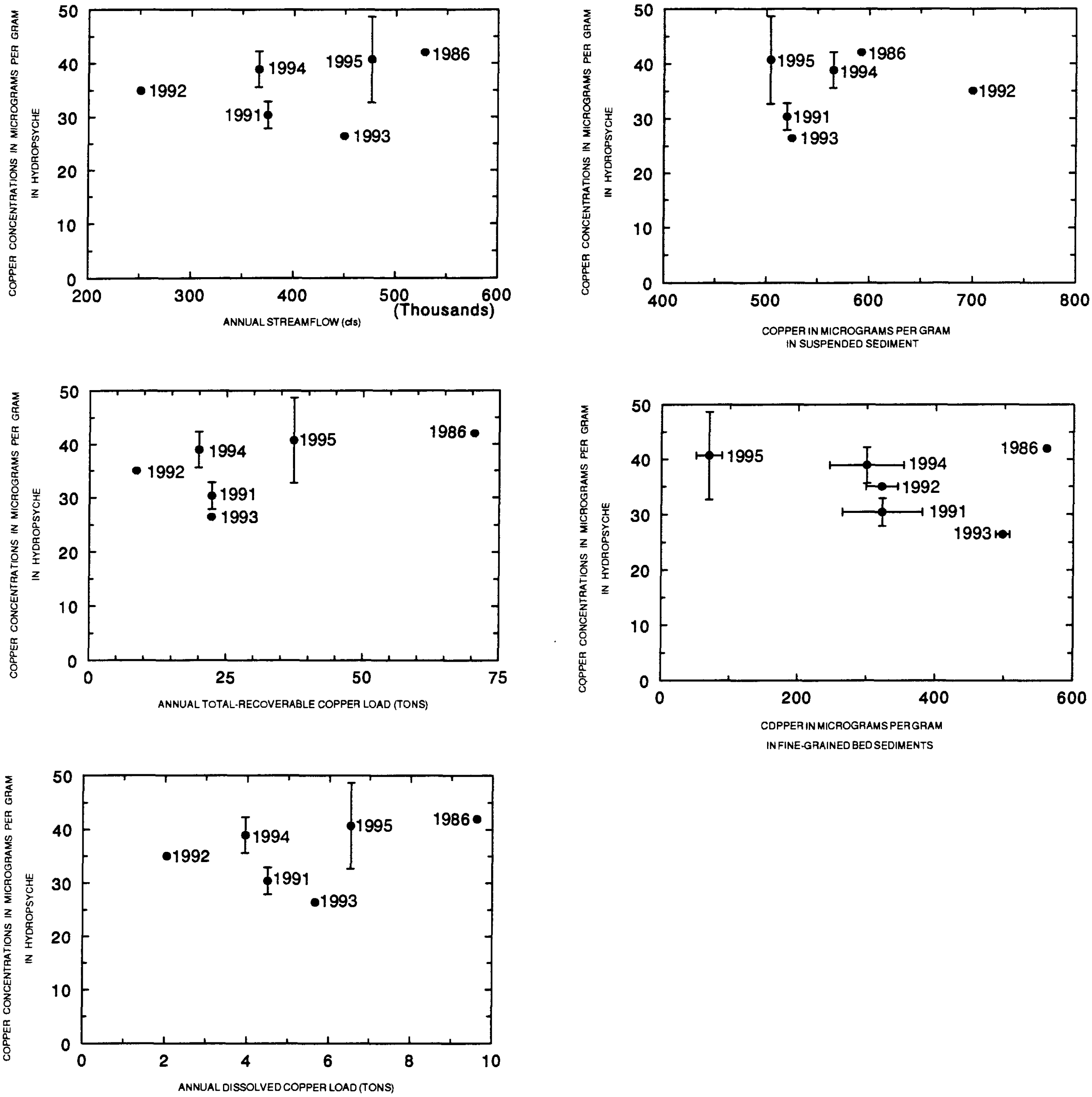


38. Relation between annual Cu concentrations in *Hydropsyche* and total annual streamflow, annual total-recoverable Cu load, annual dissolved Cu load, estimated annual Cu concentrations in suspended sediment, and Cu concentration in fine-grained bed sediment at Goldcreek. The vertical bar is the standard deviation of replicate sample values.

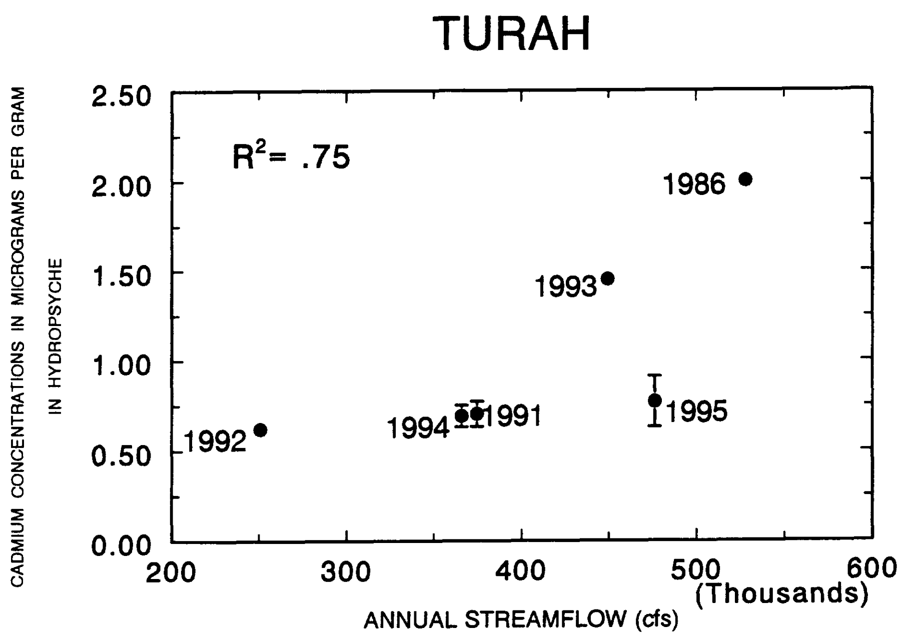


39. Relation between annual Cd concentrations in *Hydropsyche* and total annual streamflow at Goldcreek (1987 value below detection). The vertical bar is the standard deviation of replicate sample values.

TURAH



40. Relation between annual Cu concentrations in *Hydropsyche* and total annual streamflow, annual total-recoverable Cu load, annual dissolved Cu load, estimated annual Cu concentrations in suspended sediment, and Cu concentration in fine-grained bed sediment at Turah. The vertical bar is the standard deviation of replicate sample values.



41. Relation between annual Cd concentrations in *Hydropsyche* and total annual streamflow at Turah. The vertical bar is the standard deviation of replicate sample

Appendix A

CONTENTS

ILLUSTRATIONS

TABLES

ESTIMATION OF LOADS

Computational Methods

Planning for remediation requires knowledge of the locations in the upper Clark Fork basin that supply the greatest quantity of metal to the mainstem. To identify these sources, the mass of material (load) transported annually past each sampling site was estimated to determine the contributions from major tributaries and mainstem reaches. Estimates of annual loads were made utilizing the concentration data from water-quality samples, mathematical relations between variables, and daily streamflow records. Annual loads of suspended-sediment and total-recoverable copper, lead, and zinc were estimated for water years 1991-95. In addition, dissolved copper loads were estimated for the 1985-90 and 1991-95 periods.

Daily streamflow for gaging stations established in 1993 (Silver Bow Creek at Warm Springs and Clark Fork near Drummond) was estimated for the ungaged period during water years 1991-93. Missing record for Silver Bow Creek at Warm Springs was estimated by subtraction of the flow of Warm Springs Creek from the Clark Fork near Galen. Missing record for the Clark Fork near Drummond was estimated from a regression relation developed between concurrent daily streamflow at Goldcreek and near Drummond during 1993-95. The flow estimation for ungaged periods provides a complete daily streamflow record at all sampling sites for the 1991-95 period. This extension back to 1991 was necessary in order to evaluate loads for a common base period (water years 1991-95) at all of the sites.

Suspended Sediment

Suspended sediment is a key constituent used to estimate metal transport. Most of the copper, lead, and zinc in the Clark Fork is associated with sediment particles (Lambing, 1991); consequently, transport rates of metals closely reflect that of suspended sediment. Because of the strong chemical association between suspended-sediment and metals, daily values of suspended-sediment discharge were used to estimate the daily discharge of total-recoverable metals. Suspended-sediment discharge explains more of the variability in metal-transport rates than streamflow because sediment concentrations can vary seasonally for a given magnitude of flow which, in turn, directly influences the concentration of total-recoverable metal. Therefore, to ensure that seasonal differences in metal discharge were accounted for, a daily record of suspended-sediment discharge was developed for each site to estimate a daily record of metals discharge.

A daily record of suspended-sediment discharge was available for five of the sites below the Warm Springs Ponds which were operated as daily sediment stations (table 1, main body of report). At those sites, a local resident collected sediment samples at a sufficient frequency to determine a daily mean suspended-sediment concentration using methods described in Porterfield (1972). These concentrations were multiplied by the daily mean streamflow and a units-conversion constant to compute a daily suspended-sediment discharge according to the following equation:

$$Qsed = Q \times C \times K \qquad (1)$$

where:

Qsed = suspended-sediment discharge, in tons per day;
Q = streamflow, in cubic feet per second;
C = suspended-sediment concentration, in milligrams per liter;
K = units conversion constant (0.0027).

At sites other than daily sediment stations, daily sediment discharge was estimated using regression relations developed from data for periodically-collected suspended-sediment samples. Samples were collected during 1991-95 at most sites; however, five of the newly established sites were only sampled during 1993-95 (see table 1, main body of report). Instantaneous suspended-sediment discharge was computed for each sample by multiplying values of instantaneous streamflow and suspended-sediment concentration according to equation 1. Regression analysis between streamflow and suspended-sediment discharge was then used to develop a sediment-transport equation for each site.

The form of the equation used to estimate daily sediment discharge at non-daily sediment sites was evaluated by comparing estimated sediment discharge to measured sediment discharge at daily sediment stations. Results from various forms of regression equations were examined to assess how well the estimated loads reproduced the measured annual load and seasonal variability. Selection of the best data transformation for regression analysis was based on obtaining equations that were statistically significant at the 95 percent confidence level ($p<0.05$), produced residuals with constant variance about the regression line, generated a reliable seasonal distribution of loads, had evenly balanced positive and negative errors in annual mean estimates, and resulted in an estimated average annual load that was within 10 percent of the measured load. The form of equation that most accurately estimated the magnitude and seasonal characteristics of measured loads at daily sediment stations was used to estimate daily sediment loads at non-daily sites.

Regression equations describing sediment-transport relations for water years 1985-90 are presented in Lambing (1991). Equations for water years 1991-95 are presented in Appendix A, table 1. Regression plots for 1991-95 indicated that either logarithmic or square-root transformation of the data produced the best linear relation and residual distribution. In addition, seasonal equations were developed at most sites to better describe the differences in sediment transport between the valley snowmelt period (January-May) and the mountain snowmelt/rainfall period (June-December). All equations for 1991-95 are highly significant ($p <0.001$). Standard errors of estimate range from 39 to 106 percent. Although daily values of sediment discharge measured directly at daily sediment stations were used in subsequent metal-transport calculations, equations are given for all stations to provide a mathematical description of sediment transport.

Table 1 -- Equations for estimating suspended-sediment discharge, water years 1991-95. [R^2, coefficient of determination; p, significance level; SE, standard error of estimate, in percent; LOG, base 10 logarithm; SEDQ, suspended-sediment discharge, in tons per day; Q, streamflow, in cubic feet per second; <, less than]

Station	Equation	R^2	p	SE
Silver Bow Creek at Warm Springs	LOG SEDQ = $-1.16 + .133(Q)^{0.5}$	0.73	<.0001	85
Warm Springs Creek at Warm Springs:				
January-May	LOG SEDQ = $-1.09 + .185(Q)^{.5}$	.87	<.0001	65
June-December	LOG SEDQ = $-1.40 + .160(Q)^{.5}$	.92	.0006	68
Clark Fork near Galen:				
January-May	LOG SEDQ = $-.788 + .110(Q)^{.5}$	.82	<.0001	58
June-December	LOG SEDQ = $-1.17 + .120(Q)^{.5}$	94	<.0001	66
Clark Fork at Deer Lodge:				
January-May	LOG SEDQ = $-.602 + .121(Q)^{.5}$	.85	<.0001	39
June-December	LOG SEDQ = $-.745 + .113(Q)^{.5}$	.88	<.0001	74
Little Blackfoot River near Garrison:				
January-May	LOG SEDQ = $-.955 + .123(Q)^{.5}$	.91	<.0001	71
June-December	LOG SEDQ = $-1.49 + .128(Q)^{.5}$	.95	<.0001	49
Clark Fork at Goldcreek:				
January-May	LOG SEDQ = $.0977 + .0671(Q)^{.5}$	.68	<.0001	73
June-December	LOG SEDQ = $-.470 + .0730(Q)^{.5}$	.89	<.0001	106
Flint Creek near Drummond:				
January-May	SEDQ = $.00100(Q)^{1.93}$	.93	<.0001	48
June-December	SEDQ = $.00200(Q)^{1.70}$	.89	<.0001	80
Clark Fork near Drummond:				
January-May	LOG SEDQ = $.147 + .0648(Q)^{.5}$	.77	<.0001	74
June-December	LOG SEDQ = $-.337 + .0680(Q)^{.5}$	.86	<.0001	96
Rock Creek near Clinton	LOG SEDQ = $-1.03 + .0735(Q)^{.5}$	.96	<.0001	52
Clark Fork at Turah:				
January-May	LOG SEDQ = $.365 + .0428(Q)^{.5}$	.87	<.0001	55
June-December	LOG SEDQ = $-.196 + .0481(Q)^{.5}$	.91	<.0001	66
Blackfoot River near Bonner	LOG SEDQ = $-.375 + .0448(Q)^{.5}$	.93	<.0001	68
Clark Fork above Missoula:				
January-May	LOG SEDQ = $.247 + .0311(Q)^{.5}$	.95	<.0001	43
June-December	LOG SEDQ = $-.0745 + .0332(Q)^{.5}$	.95	<.0001	49

Total-Recoverable Metals

Annual total-recoverable metal loads were estimated using regression relations between suspended-sediment discharge and metal discharge at each site. The correlations were developed using data from periodic stream samples that were analyzed for both suspended-sediment and total-recoverable metal concentration. Prior to developing regression relations, the suspended-sediment and total-recoverable metal concentrations were converted to instantaneous discharge values. Suspended-sediment concentration was converted to suspended-sediment discharge as described above in equation 1. Metal concentration was converted to metal discharge by the following equation:

$$Qmetal = Q \times C \times K \qquad (2)$$

where:

Qmetal = metal discharge, in tons per day;
Q = streamflow, in cubic feet per second;
C = metal concentration, in micrograms per liter; and
K = units conversion constant (0.0000027).

After concentrations were converted to discharge, regression relations were developed between instantaneous suspended-sediment and total-recoverable metals discharge. Unlike suspended sediment, no direct measurement of daily metal loads was available to evaluate the accuracy of metals-transport equations. Therefore, the form of regression equation was selected on the basis of statistical criteria of correlation significance and uniform distribution of residuals. Examination of regression plots and regression statistics indicated that logarithmic transformation of both suspended- sediment and metal discharge provided the best linear description of metal transport.

Equations for estimating total-recoverable metal discharge at eight sites for water years 1985-90 are presented in Lambing (1991). Equations for estimating total-recoverable copper, lead, and zinc discharge at twelve sites for water years 1991-95 are presented in Appendix A, tables 2-4. All equations for 1991-95 are linear using logarithmically-transformed data and are significant ($p<0.001$). The ranges of standard errors are 31-106 percent for copper, 31-82 percent for lead, and 30-84 percent for zinc.

Table 2-- Equations for estimating total-recoverable copper discharge, water years 1991-95 [R^2, coefficient of determination; p, significance level; SE, standard error of estimate, in percent; CUQ, copper discharge, in tons per day; SEDQ, suspended-sediment discharge, in tons per day; <, less than.]

Station	Equation	R^2	p	SE
Silver Bow Creek at Warm Springs	$CUQ = .00468(SEDQ)^{0.640}$	0.73	<.001	58
Warm Springs Creek at Warm Springs	$CUQ = .000977(SEDQ)^{1.04}$	.90	<.001	68
Clark Fork near Galen	$CUQ = .00372(SEDQ)^{.787}$	.95	<.001	37
Clark Fork at Deer Lodge	$CUQ = .00214(SEDQ)^{.922}$	.96	<.001	31
Little Blackfoot River near Garrison	$CUQ = .000316(SEDQ)^{.641}$	.91	<.001	60
Clark Fork at Goldcreek	$CUQ = .00263(SEDQ)^{.784}$	.96	<.001	32
Flint Creek near Drummond	$CUQ = .000251(SEDQ)^{.813}$	.94	<.001	45
Clark Fork near Drummond	$CUQ = .00166(SEDQ)^{.840}$	.93	<.001	44
Rock Creek near Clinton	$CUQ = .000427(SEDQ)^{.742}$	.84	<.001	89
Clark Fork at Turah Bridge, near Bonner	$CUQ = .00148(SEDQ)^{.862}$	.96	<.001	32
Blackfoot River near Bonner	$CUQ = .000741(SEDQ)^{.697}$	.81	<.001	106
Clark Fork above Missoula	$CUQ = .00245(SEDQ)^{.729}$	.92	<.001	44

Table 3-- Equations for estimating total-recoverable lead discharge water years 1991-95. [R^2, coefficient of determination; p, significance level; SE, standard error of estimate, in percent; PBQ, lead discharge, in tons per day; SEDQ, suspended-sediment discharge, in tons per day; <, less than.]

Station	Equation	R^2	p	SE
Silver Bow Creek at Warm Springs	$PBQ = .000245(SEDQ)^{0.845}$	0.78	<.001	69
Warm Springs Creek at Warm Springs	$PBQ = .0000912(SEDQ)^{1.12}$	.94	<.001	53
Clark Fork near Galen	$PBQ = .000245(SEDQ)^{.904}$	.89	<.001	64
Clark Fork at Deer Lodge	$PBQ = .000174(SEDQ)^{1.01}$	.96	<.001	35
Little Blackfoot River near Garrison	$PBQ = .000166(SEDQ)^{.695}$	.88	<.001	78
Clark Fork at Goldcreek	$PBQ = .000182(SEDQ)^{.926}$	.97	<.001	31
Flint Creek near Drummond	$PBQ = .000257(SEDQ)^{.987}$	.97	<.001	40
Clark Fork near Drummond	$PBQ = .000126(SEDQ)^{1.01}$	.95	<.001	44
Rock Creek near Clinton	$PBQ = .000380(SEDQ)^{.511}$	.81	<.001	56
Clark Fork at Turah Bridge, near Bonner	$PBQ = .000174(SEDQ)^{.944}$	.95	<.001	42
Blackfoot River near Bonner	$PBQ = .000447(SEDQ)^{.642}$	.85	<.001	82
Clark Fork above Missoula	$PBQ = .000331(SEDQ)^{.802}$	.86	<.001	72

Table 4-- Equations for estimating total-recoverable zinc discharge, water years 1991-95. [R^2, coefficient of determination; p, significance level; SE, standard error of estimate, in percent; ZNQ, zinc discharge, in tons per day; SEDQ, suspended-sediment discharge, in tons per day; <, less than.]

Station	Equation	R^2	p	SE
Silver Bow Creek at Warm Springs	$ZNQ = .0107(SEDQ)^{0.614}$	0.57	<.001	84
Warm Springs Creek at Warm Springs	$ZNQ = .000955(SEDQ)^{.938}$	.89	<.001	66
Clark Fork near Galen	$ZNQ = .00676(SEDQ)^{.738}$	.87	<.001	57
Clark Fork at Deer Lodge	$ZNQ = .00263(SEDQ)^{.920}$	.95	<.001	36
Little Blackfoot River near Garrison	$ZNQ = .00151(SEDQ)^{.554}$	.87	<.001	64
Clark Fork at Goldcreek	$ZNQ = .00380(SEDQ)^{.784}$	.96	<.001	30
Flint Creek near Drummond	$ZNQ = .00129(SEDQ)^{.860}$	.92	<.001	56
Clark Fork near Drummond	$ZNQ = .00229(SEDQ)^{.888}$	.92	<.001	49
Rock Creek near Clinton	$ZNQ = .00339(SEDQ)^{.435}$	.81	<.001	50
Clark Fork at Turah Bridge, near Bonner	$ZNQ = .00295(SEDQ)^{.833}$	.93	<.001	45
Blackfoot River near Bonner	$ZNQ = .00447(SEDQ)^{.500}$	.87	<.001	51
Clark Fork above Missoula	$ZNQ = .00724(SEDQ)^{.628}$	.75	<.001	76

Dissolved Copper

Although total-recoverable metal is the focus of transport estimates in this report, the annual load of dissolved copper was examined in limited terms to allow calculation of the particulate (suspended) copper load. In addition, dissolved copper load was used as an exploratory tool to provide insights into possible accumulation patterns in the bed and biota. Copper was the element chosen for evaluation because it occurs in consistently detectable concentrations in the dissolved form at mainstem sites. This detectability prevents the statistical uncertainty associated with load estimates made from dissolved metal concentrations that commonly are below analytical detection levels.

Regression relations were developed from instantaneous values of streamflow and dissolved copper concentrations measured in periodic stream samples. In general, dissolved copper concentrations increased as flows increased. The response of dissolved copper concentration to changes in streamflow is highly variable and results in a statistically significant, but generally weak, correlation at most sites.

Dissolved copper discharge was estimated in the same manner as that for total-recoverable discharge. The instantaneous concentrations were converted to dissolved copper discharge according to equation 2. Logarithmically- transformed values of dissolved copper discharge and streamflow were used to develop a linear regression relation. To be consistent with the computation of total-recoverable metal loads, the dissolved copper data were segregated into the two study periods of 1985-90 and 1991-95. Separate regression equations were developed for each study period. This grouping of data was done so that the same base periods were used to compute both the total-recoverable and dissolved copper discharges. Commonality of base periods is necessary for temporal comparisons to ensure that the environmental and analytical conditions that existed during the various years of data collection had an equivalent effect on the data used to generate estimates. Equations for estimating dissolved copper discharge are presented in Appendix A, tables 5 and 6 for water years 1985-90 and 1991-95, respectively. The equations for 1985-90 have been adjusted for bias as described in the following section.

Table 5 .-- Equations for estimating dissolved copper discharge, water years 1985-90. [R^2, coefficient of determination; p, significance level; SE, standard error of estimate, in percent; CUQ.DIS, dissolved copper discharge, in tons per day; Q, streamflow, in cubic feet per second; <, less than. Dissolved copper concentrations measured during 1985-90 have been adjusted for analytical bias by subtracting 1 ug/L from reported values. If a value of 1 or <1 ug/L was originally reported, a value of 0.5 ug/L was used in the regression analysis.]

Station	Equation	R^2	p	SE
Clark Fork near Galen	$CUQ.DIS = .00000977(Q)^{1.25}$	.79	<.001	62
Clark Fork at Deer Lodge	$CUQ.DIS = .00000724(Q)^{1.26}$	.73	<.001	75
Little Blackfoot River near Garrison	$CUQ.DIS = .000000759(Q)^{1.30}$	.84	<.001	65
Flint Creek near Drummond	$CUQ.DIS = .00000186(Q)^{1.18}$	.78	<.001	79
Rock Creek near Clinton	$CUQ.DIS = .000000129(Q)^{1.47}$	.80	<.001	67
Clark Fork at Turah Bridge, near Bonner	$CUQ.DIS = .000000141(Q)^{1.60}$	.77	<.001	71
Blackfoot River near Bonner	$CUQ.DIS = .000000417(Q)^{1.30}$	.75	<.001	76
Clark Fork above Missoula [1]	$CUQ.DIS = .00000100(Q)^{1.24}$	.83	<.001	48

[1] No analytical adjustments were made to dissolved copper concentration at the Clark Fork above Missoula because metals samples were not collected until the 1990 water year; therefore, the equation is predominated by 1991-95 unbiased data. The 1990-95 data were used to estimate dissolved copper discharge for both the 1985-90 and 1991-95 periods.

Table 6 -- Equations for estimating dissolved copper discharge, water years 1991-95. [R^2, coefficient of determination; p, significance level; SE, standard error of estimate, in percent; CUQ.DIS, dissolved copper discharge, in tons per day; Q, streamflow, in cubic feet per second; <, less than.]

Station	Equation	R	p	SE
Silver Bow Creek at Warm Springs	$CUQ.DIS = .0000145(Q)^{1.19}$	0.82	<.001	40
Warm Springs Creek at Warm Springs	$CUQ.DIS = .00000389(Q)^{1.18}$	.82	<.001	69
Clark Fork near Galen	$CUQ.DIS = .0000102(Q)^{1.18}$	.89	<.001	42
Clark Fork at Deer Lodge	$LOG(CUQ.DIS)= -3.54 + .0802(Q)^{.5}$	.88	<.001	38
Little Blackfoot River near Garrison	$CUQ.DIS = .000000871(Q)^{1.25}$	.82	<.001	73
Clark Fork at Goldcreek	$CUQ.DIS = .00000219(Q)^{1.34}$	.85	<.001	41
Flint Creek near Drummond	$CUQ.DIS = .00000190(Q)^{1.17}$	.88	<.001	52
Clark Fork near Drummond	$LOG(CUQ.DIS)= -3.19 + .0430(Q)^{.5}$	.78	<.001	56
Rock Creek near Clinton	$LOG(CUQ.DIS)= -4.24 + .0478(Q)^{.5}$	.92	<.001	45
Clark Fork at Turah Bridge, near Bonner	$CUQ.DIS = .000000245(Q)^{1.53}$	.90	<.001	37
Blackfoot River near Bonner	$CUQ.DIS = .00000148(Q)^{1.11}$	.83	<.001	55
Clark Fork above Missoula	$CUQ.DIS = .00000100(Q)^{1.24}$	.83	<.001	48

Potential Sources of Measurement Bias and Effect on Load Estimates

When evaluating a long-term data base, it is necessary to examine whether changes in analytical or sampling methods during the period may have caused a significant shift in reported results. A methods-related shift in results could create the appearance of an environmental trend over time that is actually just an artifact of measurement bias. Examination of method changes is important, because both analytical and sampling procedures for determining metal concentrations in water have improved globally since 1985. The USGS has continually refined its protocols during the past decade to ensure that data are representative of actual environmental conditions. In particular, efforts have been made to reduce or prevent external contamination during sample handling and analysis. Such ongoing improvements may lead to a downward shift in reported concentrations.

To evaluate the effect of possible bias that may be present in older data, blank sample results and laboratory methodology changes were examined. Although QC data were limited during 1985-90, all blanks during this period consistently showed a concentration of 2-3 ug/L for total-recoverable copper (Lambing, 1991, p. 69). Dissolved copper concentrations in these blanks were at or below the detection level of 1 ug/L. The consistently higher values of total-recoverable copper compared to dissolved copper likely indicates that laboratory contamination, probably associated with the acid-digestion process used for total-recoverable determinations, introduced bias. The level of bias in field blanks is consistent with laboratory comparisons between former and current digestion methods used for total-recoverable analyses (Hoffman and others, 1996, p. 8), where the previous open-beaker digestion method showed a mean bias of 1.8 ug/L for copper. The laboratory switched its digestion process for total-recoverable metals in April 1992 to an in-bottle digestion that resulted in blanks that were essentially free of detectable concentrations for cadmium, copper, lead, and zinc (Hoffman and others, 1996).

Field sampling protocols also have changed since 1985 in response to recognition of sample contamination that can occur if certain measures are not taken to protect sample integrity. The USGS has developed extensive protocols for field collection and processing of samples that are designed to minimize trace levels of inorganic contamination (Horowitz, 1994). Many of the basic features of these new field protocols were implemented beginning in 1991-92. Full implementation of the new protocols began in 1993. In addition, requirements to collect a greater number of QC samples to quantify bias were initiated in 1993. As a result of the refinements to sampling and analytical methods, almost all field blanks after 1991 were at or below analytical detection limits for both total-recoverable and dissolved copper. Thus, measurement bias in excess of the analytical detection limit was effectively eliminated during the 1991-95 period; consequently, no adjustments to calculated metal loads were necessary for this latter period.

The decreased bias resulting from both laboratory and field improvements was examined to determine the effect on calculated copper loads. Quantifying the effect of bias on annual loads during 1985-90 can help to indicate whether any observed temporal trends in copper load are partly or entirely an artifact of methods change. Using an assumed bias of 2 ug/L in total-recoverable copper concentrations reported during 1985-90, the annual load representing this level of bias was calculated. This bias load was subtracted from the original 1985-90 copper loads to derive an "adjusted" annual total-recoverable copper load. The adjusted total-recoverable copper loads relative to the sediment loads were plotted to provide a more reliable basis for determining whether a downward shift in copper transport is occurring.

The adjusted total-recoverable copper load for the Clark Fork near Galen during 1985-90 compared to the original load (Appendix A, Fig. 1) indicates that a bias of 2 ug/L had only a minor effect on the amount of copper transported. This is presumably because 2 ug/L represents a relatively small fraction of the typical total-recoverable concentrations at this site (median of 25 ug/L, Dodge and others, 1996). In contrast, the adjusted copper load for Flint Creek is substantially lower than the original load

(Appendix A, Fig. 2), because the 2 ug/L bias represents a significant fraction of the typical total-recoverable copper concentrations (median of 7 ug/L, Dodge and others, 1996). This same effect from copper bias is noticeable for the other sites; that is, generally negligible effect on mainstem loads, but substantial decreases in copper load for the tributaries.

The other metals for which total-recoverable load estimates were made in this report, lead and zinc, showed a mean bias of 2.9 and 10.0 ug/L, respectively, using the former open-beaker digestion (Hoffman and others, 1996, p. 8). This level of bias is slightly larger than that indicated by field blanks and occasional environmental concentrations lower than the reported digestion bias. Consequently, adjustments for the 1985-90 total-recoverable loads were based on an assumed bias of 2 ug/L for lead, and 5 ug/L for zinc.

On the basis of blank samples analyzed during 1985-90, a bias correction for dissolved copper concentration may also be warranted. Because half of the blanks had concentrations at the minimum reporting level of 1 ug/L, it is possible that a portion of dissolved copper concentrations reported for stream samples prior to implementation of the new protocols were slightly high. Therefore, a bias adjustment of 1 ug/L is assumed for dissolved copper concentrations reported for 1985-90. The predominance of dissolved copper concentrations less than 1 ug/L in blanks analyzed during 1991-95 indicates that no bias adjustment is necessary for the latter period.

An additional error component that potentially could be responsible for apparent trend is a computational artifact. Because metal loads for each of the two time periods (1985-90 and 1991-95) were computed using a different set of equations, differences in estimation accuracy could be a potential source of apparent trend. But extensive assessment of the accuracy of sediment-transport estimates (Lambing, 1991 and this report, Appendix A), sample coverage of a wide range of seasonal and hydrologic conditions, and the highly significant total-recoverable metal-transport equations (Appendix A, tables 2-4) for both periods tends to indicate that potential computational error is probably minor.

A related source of measurement bias that could affect the accuracy of calculations and cause an apparent trend is the degree to which the data base represents the water-quality conditions for a given period. This factor cannot be directly quantified, but is highly dependent on adequate sample coverage of the wide range of seasonal and annual streamflow conditions. Characterization of water-quality conditions during maximum streamflows is especially important because a large proportion of the annual load may be transported during a relatively short period of time. The re-distribution of large amounts of sediment and associated metals during high flows may have a lasting effect on the aquatic environment as materials erode, disperse, and redeposit in new locations. It is clear that reliable trend interpretation requires representative, long-term environmental data to describe the complex interactions of variable hydrologic, chemical, and biological processes.

SPATIAL PATTERNS OF LOADS

Annual loads of suspended sediment, total-recoverable metals, and dissolved copper were estimated for each of the sampling stations for water years 1991-95. In addition, estimated average annual dissolved copper loads are presented for the 1985-90 period. Daily loads were summed to obtain annual loads, which were averaged to obtain average annual loads for each of the two study periods.

The spatial distribution of loads at the network of sampling sites in the upper basin is used to identify the major tributaries or mainstem reaches contributing the most sediment and metal to the Clark Fork. The source area for loads represents the entire watershed upstream from the sampling location. Consequently, the loads measured near the mouths of gaged tributaries represent the cumulative load derived from all sources within the tributary basin. Loads measured at mainstem stations can be informative in understanding the incremental downstream increases in loads. The load contributed from the intervening reach between mainstem sites is calculated as the difference in load between mainstem sites, minus the load contributed by a gaged tributary. Various sources within the intervening reach can collectively contribute to load increases, including ungaged tributaries, ground-water discharge, and sediments from the mainstem channel and flood plain. Because these individual inputs are not measured directly, it is unknown what proportion of load from intervening reaches is derived from each of the potential sources.

Estimates of annual suspended-sediment and metal loads also were used to determine the total mass of constituents discharged to Milltown Reservoir. The average annual load input to Milltown Reservoir was calculated as the sum of the average annual loads transported past the Clark Fork at Turah Bridge and the Blackfoot River near Bonner. The load output from the reservoir was determined at the Clark Fork above Missoula. Load estimates above and below Milltown Reservoir allow a mass-balance determination of the quantity of material deposited in the reservoir and the quantity moving through the reservoir to downstream reaches.

Loads measured at individual sampling sites and intervening reaches in the basin above the reservoir can be expressed as a percentage of the total load entering Milltown Reservoir (table 2, main body of report). The percentages of total load can then be compared among sites to assess the relative importance of individual source areas.

Suspended Sediment

Sediment-transport equations in Appendix A, table 1 were applied to the daily streamflow record of water years 1991-95 to generate a daily record of suspended-sediment discharge. Average annual suspended-sediment loads for water years 1991-95 are presented in Appendix A, table 7. Average annual suspended-sediment loads for water years 1985-90 are presented in Lambing (1991).

Table 7--Estimated average annual suspended-sediment loads, water years 1991-95
[Abbreviations: km, kilometer]

Location	Annual suspended-sediment load, in tons		
	Mainstem station	Tributary station	Other[1] sources
Silver Bow Creek at Warm Springs[2]	832		
Warm Springs Creek at Warm Springs		598	
Intervening reach (6.8 km)			543
Clark Fork near Galen	1,973		
Intervening reach (39.9 km)			5,426
Clark Fork at Deer Lodge	7,399		
Little Blackfoot River near Garrison		3,382	
Intervening reach (41.0 km)			4,336
Clark Fork at Goldcreek	15,117		
Flint Creek near Drummond		2,896	
Intervening reach (50.4 km)			6,895
Clark Fork near Drummond	24,908		
Rock Creek near Clinton		4,558	
Intervening reach (53.7 km)			3,449
Clark Fork at Turah Bridge, near Bonner	32,915		
Blackfoot River near Bonner		35,471	
Total input to Milltown Reservoir	68,386		
Clark Fork above Missoula	55,485		
Net deposition in (+) or loss from (-) Milltown Reservoir	+ 12,901		

[1] Includes ungaged tributaries, mainstem channel, and flood plain in the intervening reach between mainstem stations.
[2] For purposes of load routing, Silver Bow Creek is treated as a mainstem station.

Total-Recoverable Metals

Total-recoverable metal-transport equations in Appendix A, tables 2-4 were applied to the daily record of suspended-sediment discharge for water years 1991-95 to generate a daily record of total-recoverable copper, lead, and zinc discharge. Average annual total-recoverable metal loads for 1991-95 are presented in Appendix A, tables 8-10. Estimated average annual total- recoverable metal loads for 1985-90 are presented in Lambing (1991).

Table 8--Estimated average annual total-recoverable copper loads, water years 1991-95
[Abbreviation: km, kilometers]

Location	Annual copper load, in tons: Mainstem station	Tributary station	Other [1] sources
Silver Bow Creek at Warm Springs[2]	2.1		
Warm Springs Creek at Warm Springs		0.6	
Intervening reach (6.8 km)			1.2
Clark Fork near Galen	3.9		
Intervening reach (39.9 km)			7.9
Clark Fork at Deer Lodge	11.8		
Little Blackfoot River near Garrison		.3	
Intervening reach (41.0 km)			1.7
Clark Fork at Goldcreek	13.8		
Flint Creek near Drummond		.4	
Intervening reach (50.4 km)			3.6
Clark Fork near Drummond	17.8		
Rock Creek near Clinton		.7	
Intervening reach (53.7 km)			3.5
Clark Fork at Turah Bridge, near Bonner	22.0		
Blackfoot River near Bonner		4.1	
Total input to Milltown Reservoir	26.1		
Clark Fork above Missoula	24.5		
Net deposition in (+) or loss from (-) Milltown Reservoir	+ 1.6		

[1] Includes ungaged tributaries, ground-water discharge, and the mainstem channel and flood plain in the intervening reach between mainstem stations.
[2] For purposes of load routing, Silver Bow Creek is treated as a mainstem station.

Table 9--Estimated average annual total-recoverable lead loads, water years 1991-95 [Abbreviations: km, kilometer].

Location	Annual lead load, in tons		
	Mainstem station	Tributary station	Other [1] sources
Silver Bow Creek at Warm Springs [2]	0.1		
Warm Springs Creek at Warm Springs		.1	
Intervening reach (6.8 km)			.1
Clark Fork near Galen	.3		
Intervening reach (39.9 km)			1.0
Clark Fork at Deer Lodge	1.3		
Little Blackfoot River near Garrison		.2	
Intervening reach (41.0 km)			.4
Clark Fork at Goldcreek	1.9		
Flint Creek near Drummond		.7	
Intervening reach (50.4 km)			.7
Clark Fork near Drummond	3.3		
Rock Creek near Clinton		.3	
Intervening reach (53.7 km)			.5
Clark Fork at Turah Bridge, near Bonner	4.1		
Blackfoot River near Bonner		1.8	
Total input to Milltown Reservoir	5.9		
Clark Fork above Missoula	5.1		
Net deposition in (+) or loss from (-) Milltown Reservoir	+ 0.8		

[1] Includes ungaged tributaries, ground-water discharge, and the mainstem channel and flood plain in the intervening reach between mainstem stations.

[2] For purposes of load routing, Silver Bow Creek is treated as a mainstem station.

Table 10--Estimated average annual total-recoverable zinc loads, water years 1991-95
[Abbreviations: km, kilometer]

Location	Annual zinc load, in tons		
	Mainstem station	Tributary station	Other[1] sources
Silver Bow Creek at Warm Springs[2]	4.7		
Warm Springs Creek at Warm Springs		0.5	
Intervening reach (6.8 km)			1.0
Clark Fork near Galen	6.2		
Intervening reach (39.9 km)			8.1
Clark Fork at Deer Lodge	14.3		
Little Blackfoot River near Garrison		1.0	
Intervening reach (41.0 km)			4.6
Clark Fork at Goldcreek	19.9		
Flint Creek near Drummond		2.6	
Intervening reach (50.4 km)			8.9
Clark Fork near Drummond	31.4		
Rock Creek near Clinton		2.2	
Intervening reach (53.7 km)			3.9
Clark Fork at Turah Bridge, near Bonner	37.5		
Blackfoot River near Bonner		9.0	
Total input to Milltown Reservoir	46.5		
Clark Fork above Missoula	40.8		
Net deposition in (+) or loss from (-) Milltown Reservoir	+ 5.7		

[1] Includes ungaged tributaries, ground-water discharge, and the mainstem channel and flood plain in the intervening reach between mainstem stations.

[2] For purposes of load routing, Silver Bow Creek is treated as a mainstem station.

Dissolved Copper

Dissolved-copper transport equations in Appendix A, tables 5 and 6 were applied to the daily streamflow record for water years 1985-90 and 1991-95, respectively, to compute a daily record of dissolved copper load. The daily loads then were summed to provide an annual dissolved copper load for each year. Average annual loads of dissolved copper for the 1985-90 and 1991-95 periods are presented in Appendix A, tables 11 and 12.

Table 11-- Estimated average annual dissolved copper loads, water years 1985-90. Loads have been adjusted for analytical bias of 1 ug/L. [Abbreviations: km, kilometer]

Location	Annual copper load, in tons		
	Mainstem station	Tributary station	Other [1] sources
Clark Fork near Galen	1.20		
Intervening reach (39.9 km)			1.21
Clark Fork at Deer Lodge	2.41		
Little Blackfoot River near Garrison		.15	
Flint Creek near Drummond		.16	
Rock Creek near Clinton		.32	
Intervening reach (145.1 km)			1.94
Clark Fork at Turah Bridge	4.98		
Blackfoot River near Bonner		2.00	
Total input to Milltown Reservoir	6.98		
Clark Fork above Missoula	5.97		
Net gain in (+) or loss from (-) Milltown Reservoir	+ 1.01		

[1] Includes ungaged tributaries, ground-water discharge, and the mainstem channel and flood plain in the intervening reach between mainstem stations.

Table 12-- Estimated average annual dissolved copper loads, water years 1991-95 [Abbreviations: km, kilometer].

Location	Annual copper load, in tons		
	Mainstem station	Tributary station	Other[1] sources
Silver Bow Creek at Warm Springs[2]	1.07		
Warm Springs Creek at Warm Springs		.15	
Intervening reach (6.8 km)			.00
Clark Fork near Galen	1.19		
Intervening reach (39.9 km)			.78
Clark Fork at Deer Lodge	1.97		
Little Blackfoot River near Garrison		.15	
Intervening reach (41.0 km)			.73
Clark Fork at Goldcreek	2.85		
Flint Creek near Drummond		.16	
Intervening reach (50.4 km)			.18
Clark Fork near Drummond	3.19		
Rock Creek near Clinton		.31	
Intervening reach (53.7 km)			1.04
Clark Fork at Turah Bridge, near Bonner	4.54		
Blackfoot River near Bonner		1.54	
Total input to Milltown Reservoir	6.08		
Clark Fork above Missoula	5.79		
Net deposition in (+) or loss from (-) Milltown Reservoir	+ .29		

[1] Includes ungaged tributaries, ground-water discharge, and the mainstem channel and flood plain in the intervening reach between mainstem stations.

[2] For purposes of load routing, Silver Bow Creek is treated as a mainstem station.

TEMPORAL PATTERNS

Annual Suspended-Sediment and Total-Recoverable Copper Loads

Annual loads of suspended sediment and total-recoverable copper were plotted together to indicate the concurrent pattern of fluctuation over time. Plots of annual loads during 1985-95 for additional sites not shown in the main body of the report or in the examples of bias adjustment (Appendix A, Fig. 1 and 2) are presented in Appendix A, figures 3-6. Loads for 1985-90 in these graphs have been bias adjusted, with the exception of the Clark Fork above Missoula, as previously noted.

Annual Streamflow and Dissolved Copper Loads

Annual streamflow volume and dissolved copper loads were plotted together to indicate the concurrent pattern of fluctuation over time. Plots of streamflow and dissolved copper load during 1985-95 for sites not shown in the main body of the report are presented in Appendix A, figures 7-13. Loads for 1985-90 have been bias adjusted, with the exception of Clark Fork above Missoula.

ESTIMATION OF ANNUAL CONCENTRATION FROM ANNUAL LOADS

Annual loads offer insight into how metal transport varies with annual flow. Metals move through the system predominantly in short-duration pulses in response to runoff and the available supply of metals. Because annual loads represent the quantity of metal passing through the aquatic habitat of biota, they may indicate relative differences in exposure from year-to-year. Another way to evaluate annual differences in exposure is to convert annual loads and flow into a mass:volume ratio equivalent to an annual concentration representing cumulative conditions during the year. A time-integrated concentration calculated from annual loads may serve as a surrogate indicator of biological exposure to metal. Such metal concentrations can be compared between years and between sites to assess overall differences in potential metal exposure. Annual concentrations calculated in this manner do not provide information on the range or duration of instantaneous concentrations; therefore, they cannot be used to assess exceedances of aquatic-life criteria. But annual concentrations may be a useful way to indicate a composite average condition to assess relative differences in exposure.

Total-recoverable copper concentration in surface water

Annual total-recoverable copper loads, in tons, were divided by annual streamflow volumes, in acre-feet, and multiplied by a unit-conversion factor to derive a mass:volume ratio equivalent to ug/L. A summary of estimated annual total-recoverable copper concentrations for 1985-95 is presented in Appendix A, table 13. Concentrations for 1985-90 were computed from loads adjusted for bias as described earlier.

Table 13.-- Estimated annual total-recoverable copper concentrations in surface water, water years 1985-95 [Total-recoverable copper concentrations for 1985-90 have been adjusted for an analytical bias of 2 ug/L].

Station	Total-recoverable copper concentration, in ug/L										
	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995
					MAINSTEM						
Clark Fork near Galen	46	50	36	40	45	40	29	20	28	23	45
Clark Fork at Deer Lodge	57	73	44	41	74	36	67	46	54	42	70
Clark Fork at Goldcreek	--	--	--	--	--	--	32	23	30	29	47
Clark Fork near Drummond	--	--	--	--	--	--	31	19	28	28	44
Clark Fork at Turah Bridge	34	47	17	22	40	28	22	13	18	20	29
Clark Fork above Missoula	9	10	13	10	10	8	13	8	10	9	13
					TRIBUTARIES						
Silver Bow Creek	--	--	--	--	--	--	27	27	18	28	32
Warm Springs Creek	--	--	--	--	--	--	13	8	20	13	15
Little Black-foot River	2	4	2	2	4	4	2	1	2	2	3
Flint Creek	8	10	7	6	7	7	4	4	4	5	5
Rock Creek	1	2	1	1	2	2	2	1	2	1	2
Blackfoot River	5	5	4	4	5	4	4	2	3	3	3

Dissolved copper concentration in surface water

Annual loads of dissolved copper, in tons, were divided by annual streamflow volumes, in acre-feet, and multiplied by a units-conversion factor to obtain a dissolved copper concentration equivalent to ug/L. A summary of estimated annual dissolved copper concentrations is presented in Table 14. Concentrations for 1985-90 were computed from loads adjusted for measurement bias as described earlier.

Table 14 -- Estimated annual dissolved copper concentrations in surface water, water years 1985-95 [Dissolved copper concentrations for 1985-90 have been adjusted for an analytical bias of 1 ug/L].

Station	Dissolved copper concentration, in ug/L										
	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995
MAINSTEM											
Clark Fork near Galen	13	13	11	12	12	12	10	8	10	9	10
Clark Fork at Deer Lodge	12	13	12	11	12	11	9	7	9	8	12
Clark Fork at Goldcreek	--	--	--	--	--	--	7	5	7	7	8
Clark Fork near Drummond	--	--	--	--	--	--	6	4	5	5	4
Clark Fork at Turah Bridge	4	6	4	4	5	5	4	3	5	4	5
Clark Fork above Missoula	3	3	2	2	3	3	3	2	3	2	3
TRIBUTARIES											
Silver Bow Creek	--	--	--	--	--	--	13	11	14	13	14
Warm Springs Creek	--	--	--	--	--	--	4	2	4	2	4
Little Black-foot River	1	1	1	1	1	2	1	1	1	1	1
Flint Creek	2	2	2	1	1	1	2	2	2	2	2
Rock Creek	1	1	<1	1	1	1	1	<1	1	1	1
Blackfoot River	2	2	1	1	2	2	1	1	1	1	1

Copper concentration in suspended sediment

Annual dissolved copper loads were subtracted from annual total- recoverable copper loads to determine annual loads of suspended copper in water. These annual loads of suspended copper were divided by the annual loads of suspended sediment, and multiplied by a units-conversion factor to derive an annual solid-phase copper concentration in suspended sediment. A summary of estimated annual copper concentrations in suspended sediment for 1985-95 is presented in Appendix A, table 15. Concentrations for 1985-90 were computed from loads adjusted for bias as described earlier.

Table 15 -- Estimated annual copper concentrations in suspended sediment, water years 1985-95 [Annual copper concentrations for 1985-90 have been adjusted to account for analytical bias of 2 ug/L for total-recoverable copper and 1 ug/L for dissolved copper.]

	Copper concentration, in ug/g of suspended sediment										
Station	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995
MAINSTEM											
Clark Fork near Galen	2,190	1,830	2,820	2,330	2,030	2,420	1,500	2,230	1,440	1,610	1,180
Clark Fork at Deer Lodge	1,120	989	1,120	1,140	1,010	1,040	1,320	1,500	1,330	1,350	1,260
Clark Fork at Goldcreek	--	--	--	--	--	--	795	1,150	792	881	581
Clark Fork near Drummond	--	--	--	--	--	--	598	760	621	655	519
Clark Fork at Turah	809	592	852	882	690	732	520	700	525	565	504
Clark Fork above Missoula	362	255	426	512	187	232	283	537	344	404	329
TRIBUTARIES											
Silver Bow Creek	--	--	--	--	--	--	1,698	3,299	915	1,803	905
Warm Springs Creek	--	--	--	--	--	--	746	687	883	846	749
Little Black-foot River	161	127	217	168	91	90	38	97	34	43	26
Flint Creek	151	103	152	179	154	150	107	113	98	99	94
Rock Creek	42	37	36	38	42	44	68	137	78	98	72
Blackfoot River	136	132	210	197	79	89	62	101	72	75	81

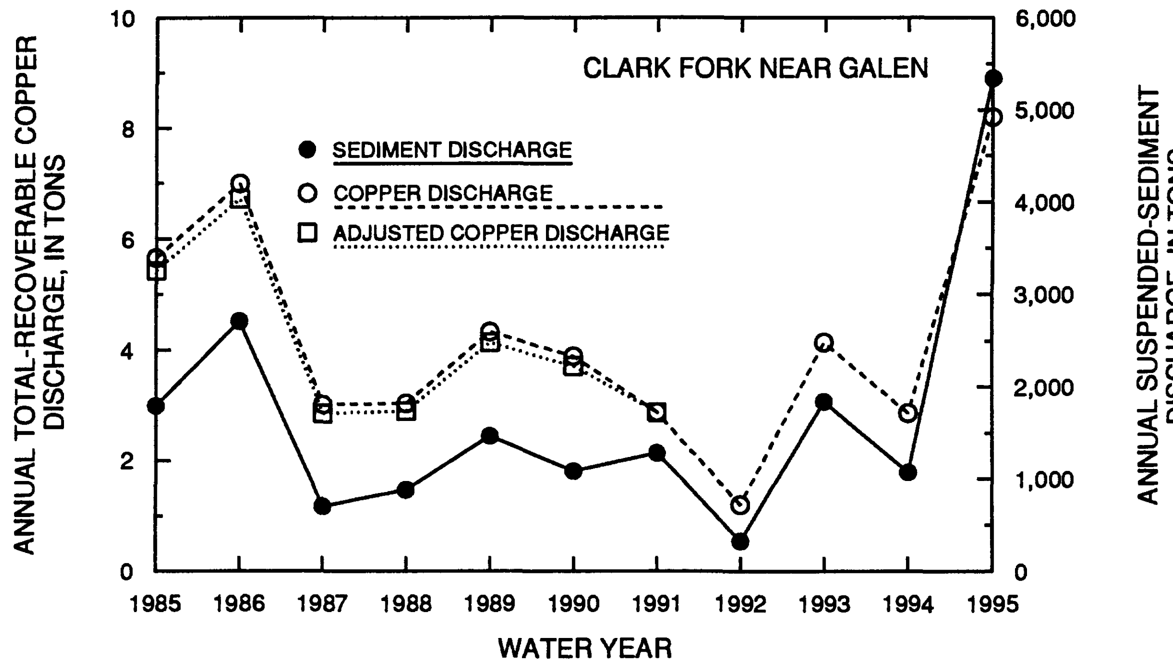


Figure A-1. Annual suspended-sediment and total-recoverable copper discharge for the Clark Fork near Galen, water years 1985-95, with bias adjustment illustrated for water years 1985-90.

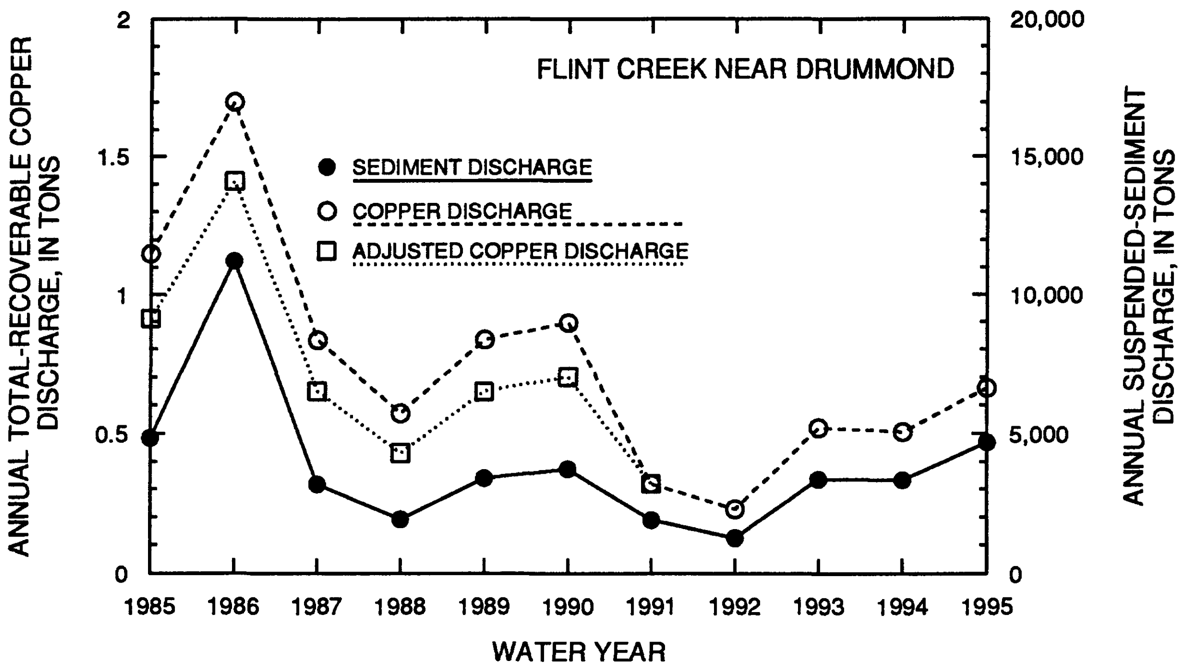


Figure A-2. Annual suspended-sediment and total-recoverable copper discharge for Flint Creek near Drummond, water years 1985-95, with bias adjustment illustrated for water years 1985-90.

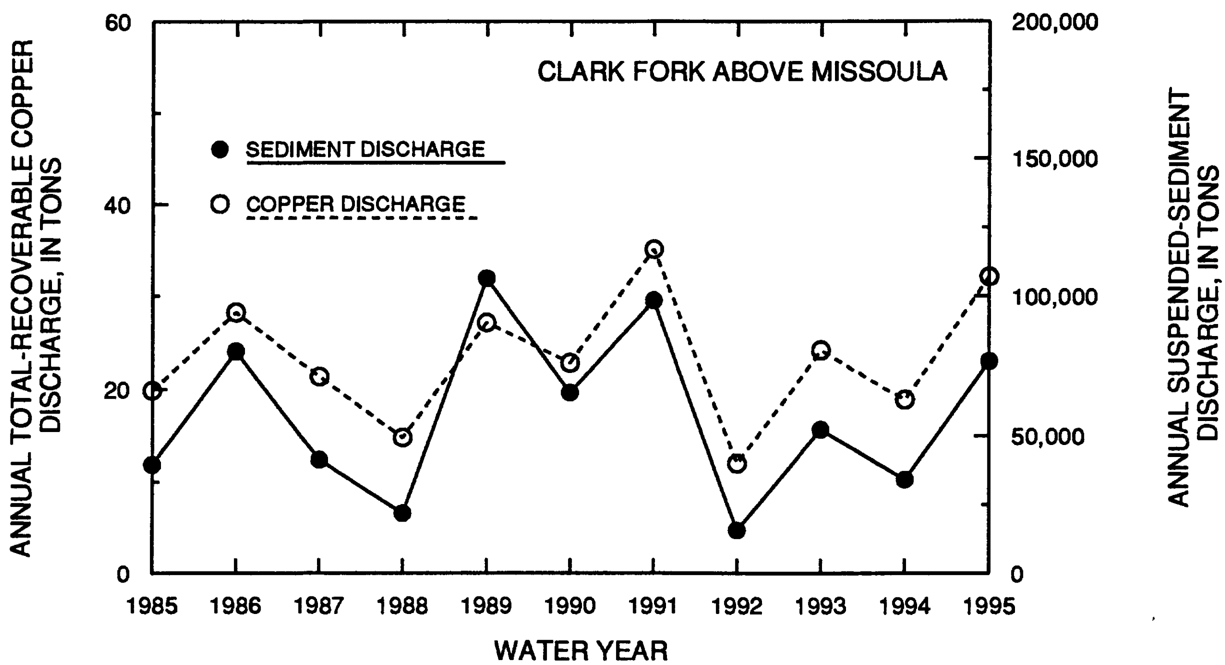


Figure A-3. Annual suspended-sediment and total-recoverable copper discharge for the Clark Fork above Missoula, water years 1985-95.

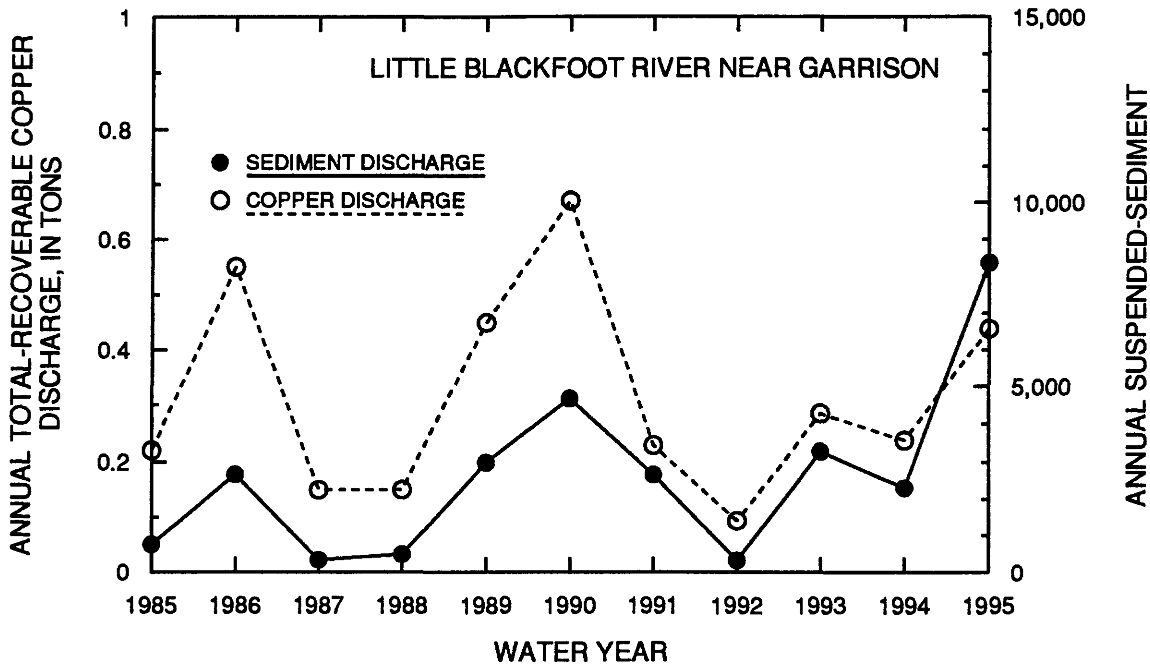


Figure A-4. Annual suspended-sediment and total-recoverable copper discharge for the Little Blackfoot River near Garrison, water years 1985-95.

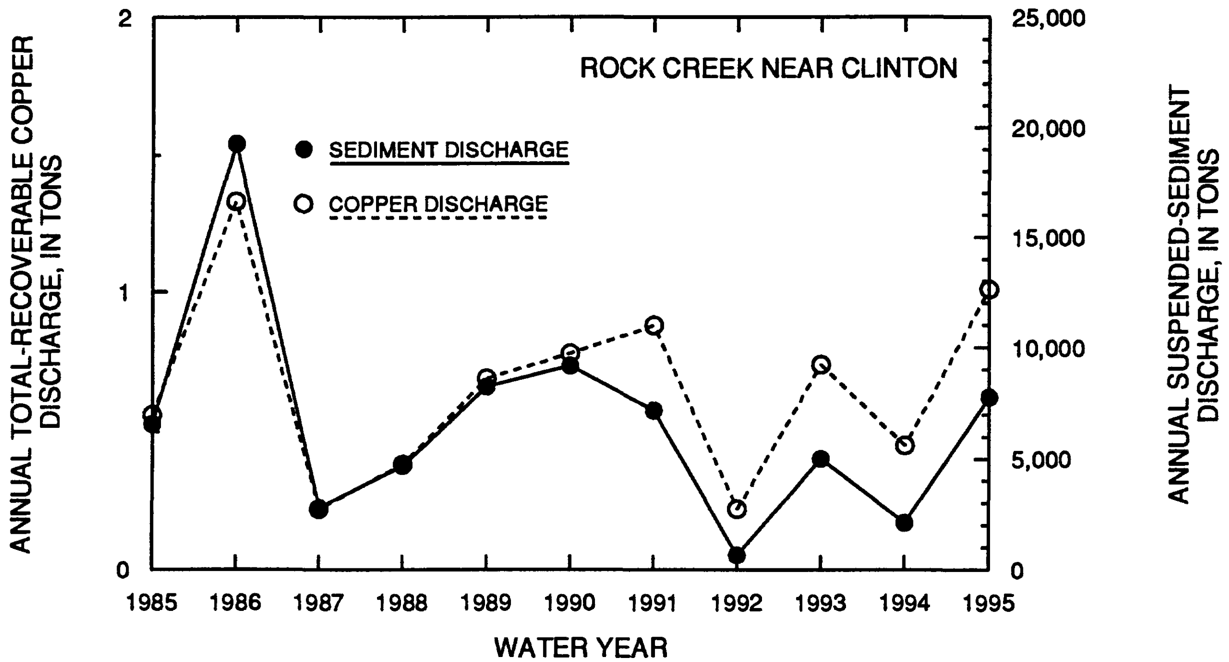


Figure A-5. Annual suspended-sediment and total-recoverable copper discharge for Rock Creek near Clinton, water years 1985-95.

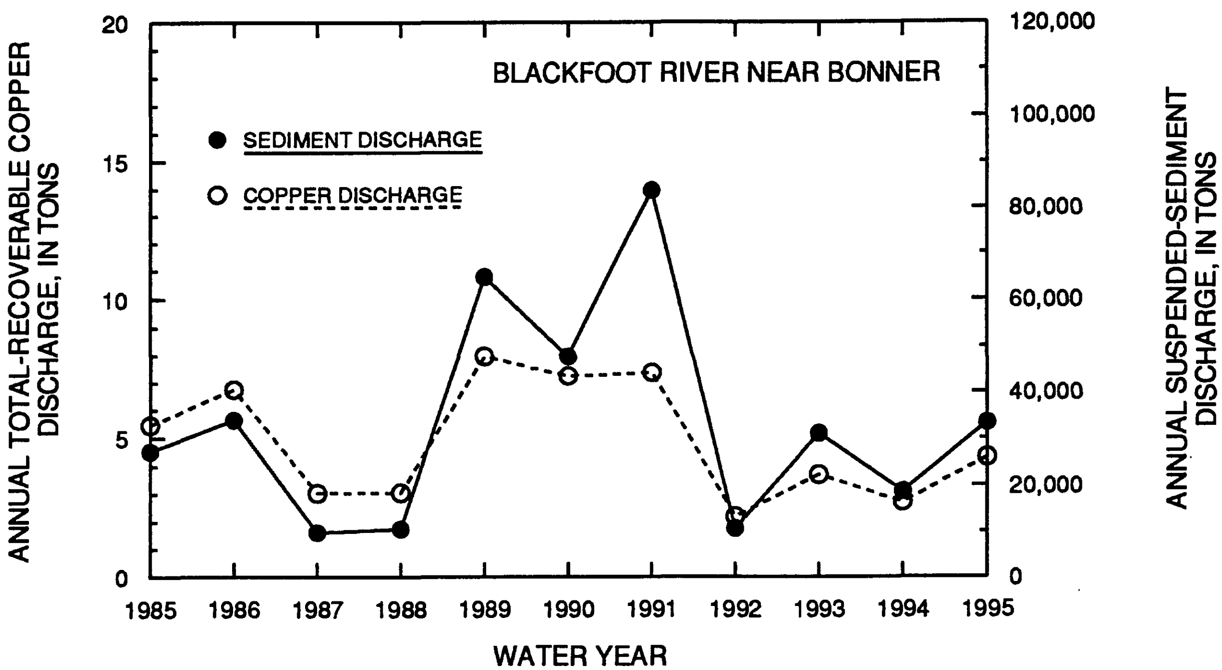


Figure A-6. Annual suspended-sediment and total-recoverable copper discharge for the Blackfoot River near Bonner, water years 1985-95.

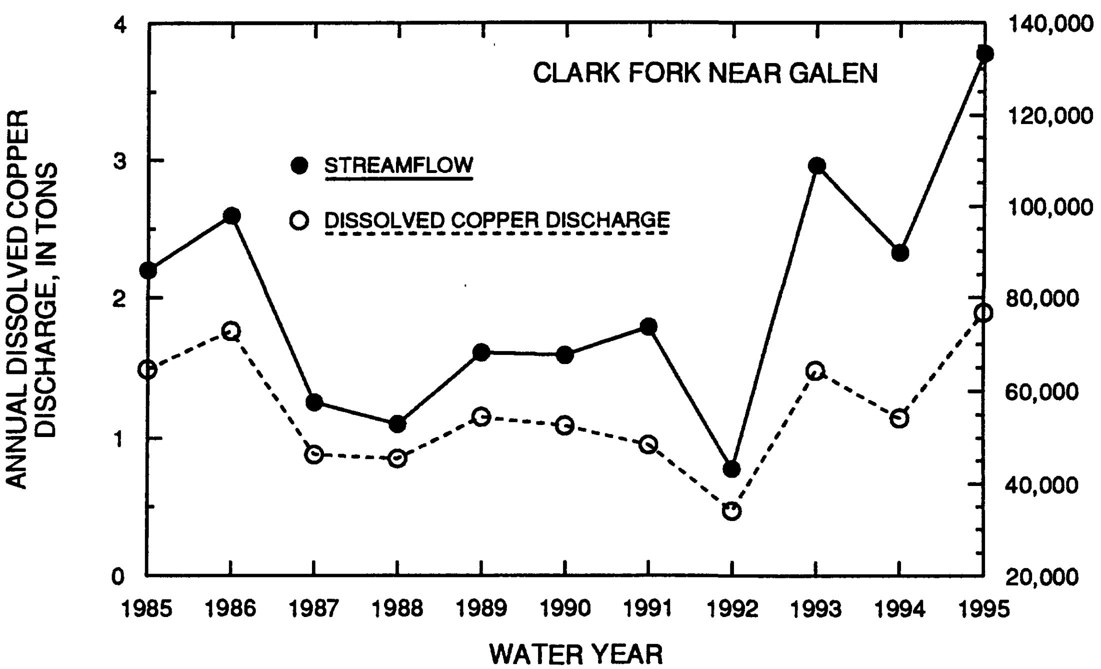


Figure A-7. Annual streamflow and dissolved copper discharge for the Clark Fork near Galen, water years 1985-95.

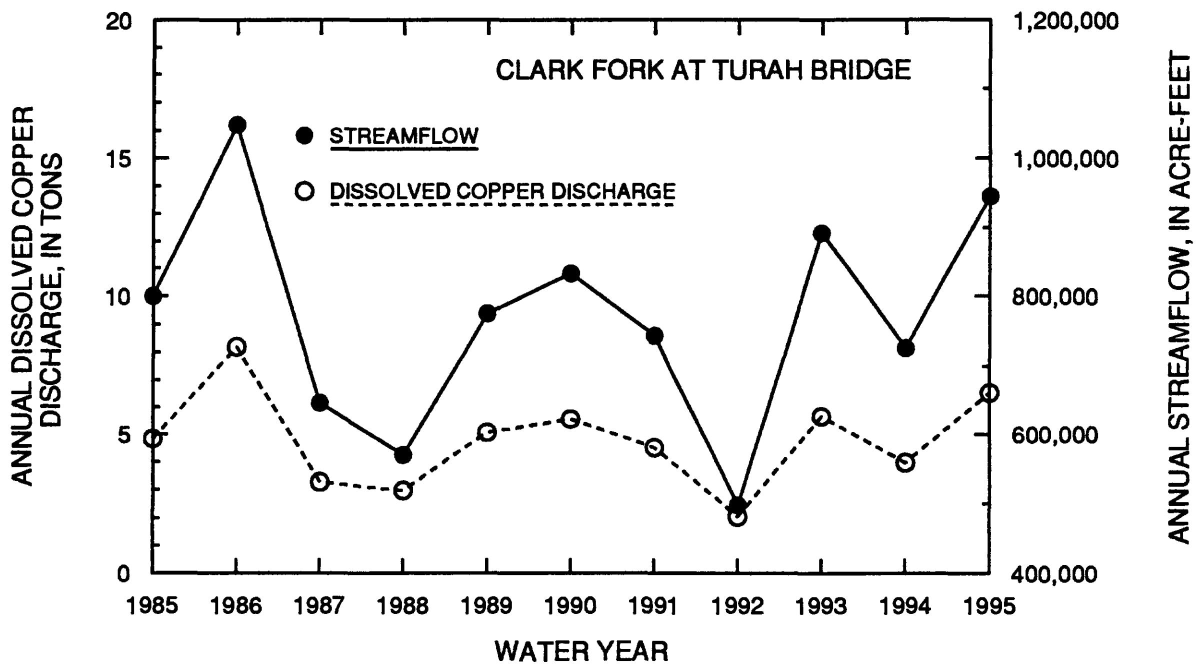


Figure A-8. Annual streamflow and dissolved copper discharge for the Clark Fork at Turah Bridge, water years 1985-95.

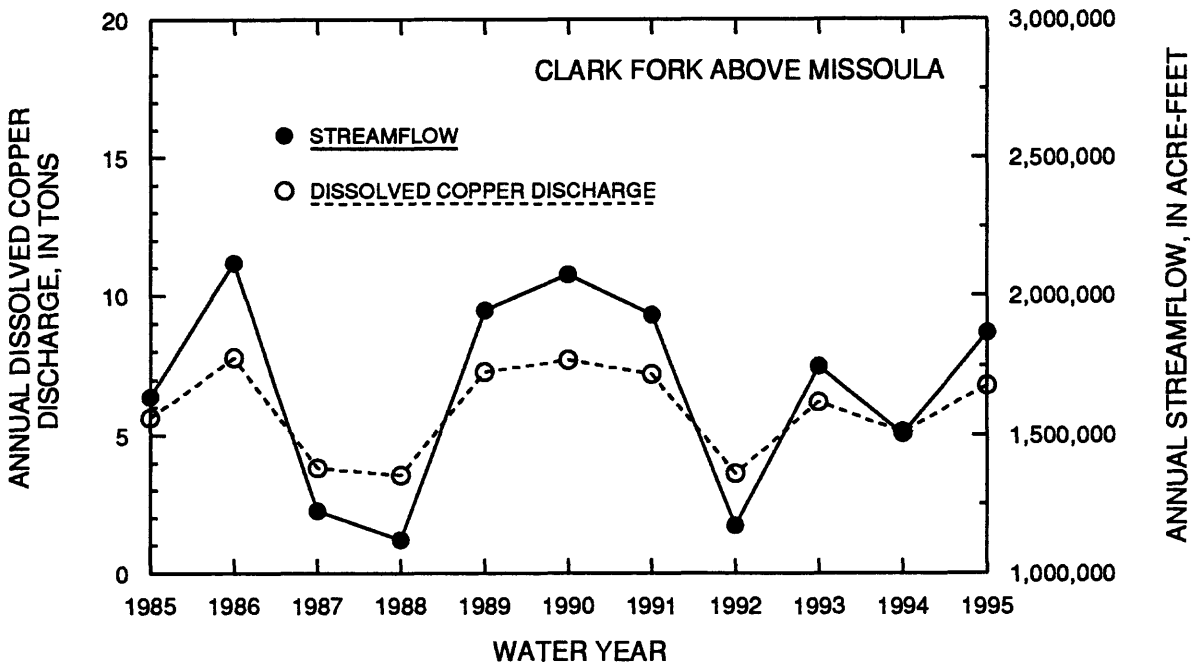


Figure A-9. Annual streamflow and dissolved copper discharge for the Clark Fork above Missoula, water years 1985-95.

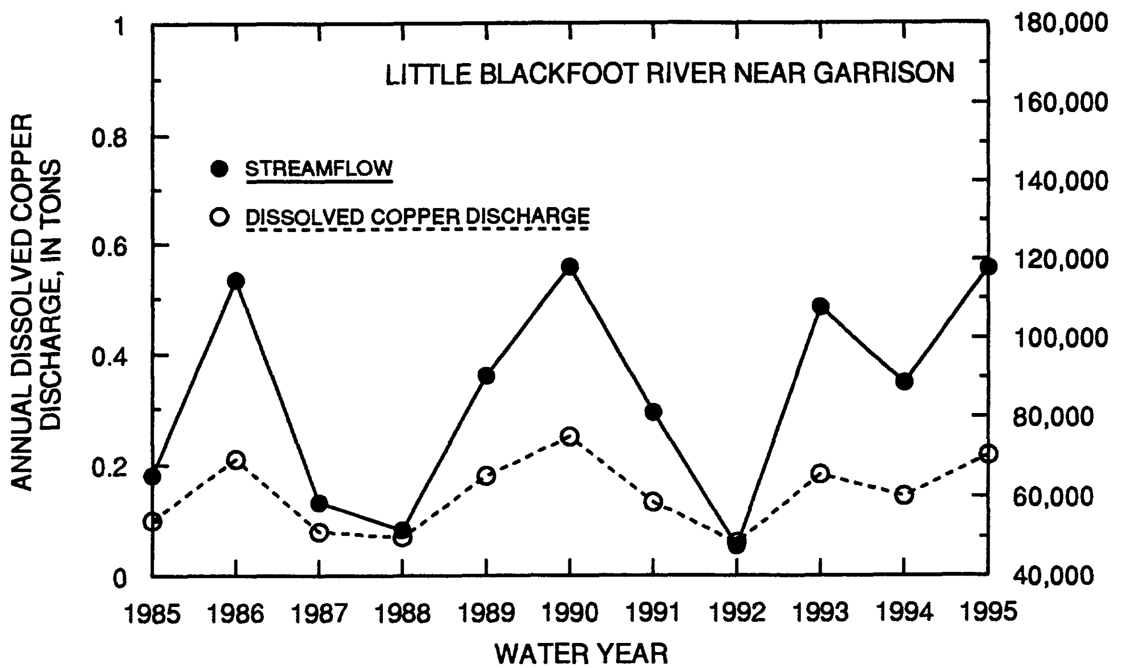


Figure A-10. Annual streamflow and dissolved copper discharge for the Little Blackfoot River near Garrison, water years 1985-95.

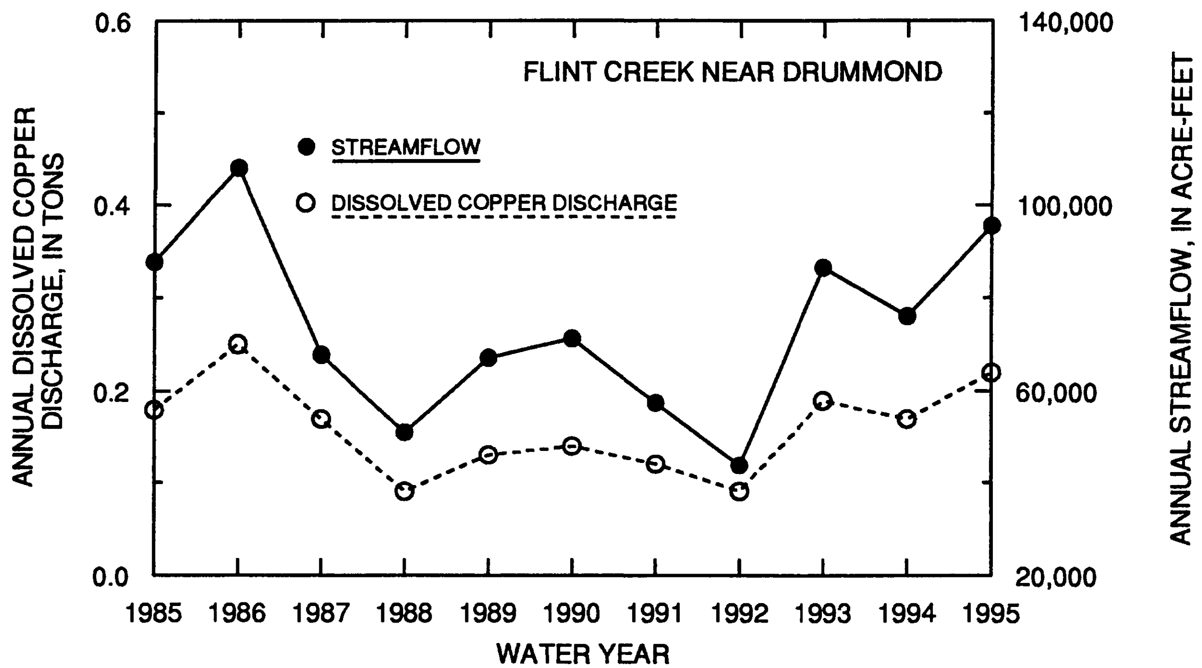


Figure A-11. Annual streamflow and dissolved copper discharge for Flint Creek near Drummond, water years 1985-95.

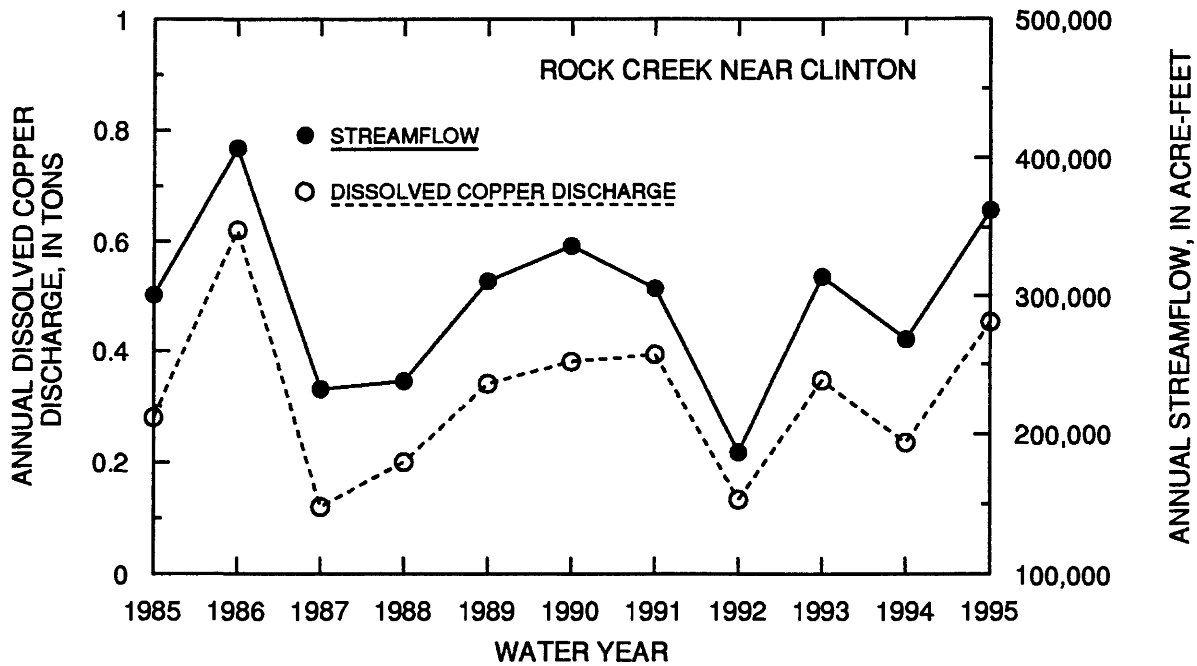


Figure A-12. Annual streamflow and dissolved copper discharge for Rock Creek near Clinton, water years 1985-95.

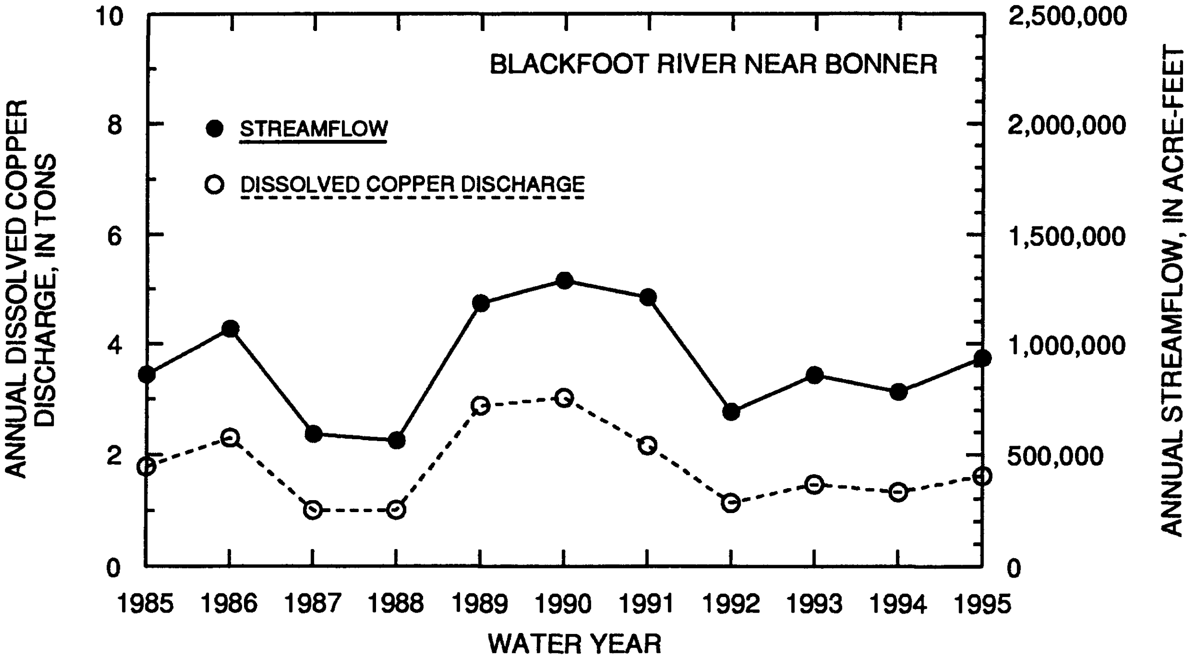


Figure A-13. Annual streamflow and dissolved copper discharge for the Blackfoot River near Bonner, water years 1985-95.