HEAVY METALS PARTITIONING IN A STREAM RECEIVING URBAN RUNOFF

by

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I. INTRODUCTION

Recent water shortages across the country, on both the nation's East and West coasts, have once again demonstrated society's utter dependence upon its most precious resource. Varying degrees of water restrictions imposed upon the residents in these drought-stricken areas interfered with the quality of life many of these people were accustomed to living. Although no one was deprived of water for his most basic needs, the experiences serve to point out the indispensability of water and the fact that society is not blessed with an unending supply of the precious liquid. This is especially apparent when one considers the growing population that will require even more water in the near future. Yet, society must not only ensure an ample quantity of water, but must also ensure a high-quality water for future users.

In the past, the major thrust to improve the water quality of the nation's streams and rivers has emphasized treatment of point sources such as municipal and industrial waste discharges. Consequently, as point sources exert less of an impact upon water quality through improved treatment techniques, non-point sources begin to exert more of an impact upon water quality and become increasingly important when considering water pollution abatement plans for a particular watershed. In fact, one must decide if, indeed, advanced wastewater treatment of point sources is marginally beneficial when non-point sources continue to degrade the water quality. Decisions of this nature become especially important in light of recent studies (1) demonstrating that non-point pollution may contribute up to one-half the total pollutional load within a particular watershed.

Non-point sources of pollution are varied and can include: precipitation; irrigation return flows; and forested, agricultural, and urban runoff. However, investigators have found the urban runoff fraction to be particularly objectionable because it contains hundreds of milligrams per liter suspended sediment, coliforms in excess of safe limits, large quantities of nutrients and organic matter, and very high concentrations of hydrocarbons and heavy metals (2). The heavy-metals fraction associated with urban stormwater can be particularly troublesome because, at high concentrations, these metals are toxic to most aquatic organisms. Typically, the heavy metals--lead, zinc, and copper--resulting from automobile emissions and tire wear have been associated with urban runoff.

Heavy metals in urban runoff eventually find their way into a receiving stream where they can either remain in the water column or be adsorbed onto the sediment or detritus and thus be effectively prevented from further travel downstream. As such, the metals would then be available for uptake by benthic organisms and could eventually be accumulated in organisms at higher trophic levels. However, subsequent storms and related high flows or changing physical-chemical conditions could resuspend the metals into the water column for further downstream movement. Thus, the partitioning of heavy metals in a stream may indicate the extent metals will be carried further downstream. Knowing the extent of downstream movement may be very important if, for instance, the stream feeds an impoundment used as a drinking water source.

The purpose of the study described in this thesis was to determine the extent of partitioning of selected toxic heavy metals between the water, sediment, detritus, and certain benthic organisms in a stream that receives considerable urban runoff. Bull Run, which forms the boundary for Prince William and Fairfax counties and flows through the city of Manassas in Northern Virginia, was selected as the site for this study because it receives only sewage treatment plant effluent and urban runoff below Manassas with little or no discharges from industrial sources. Additionally, Bull Run is a major tributary to the Occoquan reservoir, a major drinking water source. This reservoir supplies potable water for approximately 600,000 Fairfax County residents and has developed taste-and-odor problems caused by a progressing state of eutrophication. In addition to the water quality problems plaguing the reservoir, the dry weather of 1977 caused severe water shortages, requiring mandatory water restrictions to be imposed upon the system's users. The result of this study, therefore, should be useful in determining how heavy metals derived from urban runoff will affect the water quality and the aquatic organisms of a stream that feeds a water supply reservoir.

II. LITERATURE REVIEW

Urban Runoff as a Pollutant

Because of the large quantity and variety of pollutant materials found in and around urban areas, urban runoff can become a major factor in deteriorating the water quality of nearby streams and rivers. Sartor *et al*. (3), collected contaminant materials from street surfaces of twelve U.S. cities and, generally, found the material to be highly contaminated. The investigators found that the major constituent of street-surface contaminants was inorganic, mineral-like matter similar to fine sand or silt and that the overall pollutional potential was associated with the fine, inorganic solid fraction. Table 1 shows the amount of contaminant materials found on street surfaces. As can be seen, significant amounts of heavy metals, especially Zn, Pb, and Cu were collected.

The possible sources for these contaminants are many and varied. Kluesener and Lee (4) believed that some of the possible sources of nutrients in urban runoff include precipitation, dust fall, leachings from living vegetation, street litter, lawn and garden fertilizer, dead vegetation, and gasoline combustion products. The author also believed that the majority of ammonia nitrogen and one-third of nitrate nitrogen present in urban runoff originate in rainfall with the balance coming from other sources. Phosphorus, on the other hand, can originate from leachings of living vegetation and from lead halophosphate present in automobile exhausts.

Table 1

Quantity and Characteristics of Contaminants Found on Street Surfaces

[after Sartor *et al*. (3)]

Contaminant Material	Weighted Mean, lb/curb mile*
Total Solids	1,400
BOD_5	13.5
COD	95
Volatile Solids	100
Phosphates	1.1
Nitrates	0.094
Kjeldahl Nitrogen	2.2
Zinc	0.65
Copper	0.20
Lead	0.57
Nickel	0.05
Mercury	0.073
Chromium	0.11
p, p-DDD	67×10^{-6}
p, p-DDT	61×10^{-6}
Dieldrin	24×10^{-6}
PCB	$1,100 \times 10^{-6}$
Total Coliforms, organisms/curb mile	99×10^{9}
Fecal Coliforms, organisms/curb mile	5.6×10^{9}

*Except where noted.

Lagerwerff and Specht (5), in their study of Cd, Ni, Pb, and Zn contained in roadside soil and vegetation, noted a decrease in nitrogen,phosphorus, and halides with distance from traffic and suggested that phosphate and ammonia-halides were deposited with lead from car exhausts. As such, gasoline combustion products constitute the major source for Pb. Also, the use of Ni in gasoline and nickel-containing automobile parts may be a source for this heavy metal. The authors also reported that motor oils and tires are possible sources of Cd and Zn and can account for large quantities of these metals present on street surfaces.

Once deposited on street surfaces, these contaminants are available to be washed into a receiving stream during a storm. It is estimated that runoff will occur with rainfall accumulation of more than 0.1 inch (4). The amount, concentration, and travel time of contaminants found in runoff are controlled by many factors. Weibel _et al_. (6) noted that for his particular watershed, runoff usually lagged rainfall by 10 minutes. Kluesener and Lee (4) found a first-flush effect for suspended solids and the associated sorbed nutrients, nitrogen and phosphorus. Whipple and Hunter (7) also found that Pb, Zn, and Cu exhibited a first-flush effect with the metals reaching their greatest concentrations in the first 30 minutes of a storm. Some investigators, such as Garland (8), have indicated a positive relationship between urban runoff pollutant loadings and antecedent dry weather periods. This view, however, has recently been challenged in light of recent data that demonstrated a poor relationship between higher pollutant loadings and longer antecedent dry weather periods (7).

It is now generally recognized that urban runoff is a significant factor affecting the deterioration of water quality for streams draining urban areas. As early as 1964, Weibel et al. (6) concluded that urban runoff from residential and light-commercial areas in Cincinnati contributed a significant portion of pollutants to the receiving water. In fact, when comparing stormwater with raw sewage, the authors found that stormwater contributed 140 percent of the suspended solids, 44 percent of the volatile suspended solids, 25 percent of the COD, 6 percent of the BOD, 9 percent of the phosphate, and 11 percent of the nitrogen. If one compared the annual stormwater BOD load with that from secondary effluent, the percentage contributed by stormwater would increase to 60 percent.

In 1970, Bryan (9) also concluded that urban stormwater was a significant source of pollutional constituents to receiving streams in North Carolina. However, he also noted that stormwater contributions were significant when compared on a mean annual basis but were made in slugs to the receiving stream. Again, he found a relatively large annual yield percentage of COD and BOD contributed by urban stormwater to be 110 and 15 percent, respectively, that of sewage.

Likewise, Colston (10) in 1974, found that the organic content in urban stormwater for Durham, North Carolina was approximately one-half that of typical raw wastewater, whereas that of suspended solids was two to fifty times as great. Colston further concluded that during wet periods, yields of organics (as COD) were four and one-half times that of raw sewage, while suspended solids yields were 100 times as great. Moreover, Colston concluded that for 20 percent of the time, downstream water quality was affected by urban runoff.

Randall et al. (11) concluded that organic and nutrient contributions from urban runoff in the Occoquan, Virginia watershed contributed a sizeable fraction of the total pollution entering Bull Run. Again, pollutant contributions from urban runoff were significant when compared to contributions from secondary effluent. Percentage loading contributions from urban runoff for TOC, suspended solids, total nitrogen, and total phosphorus were found to be 48, 98, 20, and 24 percent, respectively.

Heavy Metals in Urban Runoff

One aspect of urban runoff that concerns many is the presence of toxic heavy metals such as Pb, Zn, Cu, Cd, Ni, and Cr. As demonstrated by Sartor's (3) investigation, considerable amounts of Zn, Pb, Cu, and Cr were found on street surfaces, along with trace amounts of Hg and Ni. Additionally, 48.7 percent of these pollutants were associated with the fine sand fraction (greater than 246μ) while 51.2 percent were associated with the silt-clay fraction (less than 246μ). Because most of the metal content was associated with such small-sized particles, it was found that present street cleaning methods are ineffective in removing these pollutants from street surfaces.

Heavy metals present on street surfaces pose a potential threat to organisms living near a highway. In the study conducted by

Lagerwerff and Specht (5), concentration of Cd, Ni, Pb, and Zn in roadside soil and grass samples decreased with distance from traffic and with depth in the soil profile. Cadmium concentrations 8 m from the road were 0.75 mg/Kg in the grass and 0.94 mg/Kg in the top 5 cm of soil. Likewise, Ni, Pb, and Zn concentrations in grass and soil were 3.8, 74; 51.3, 540; and 40, 162 mg/Kg, respectively. No relationship could be found among the various metals in the soil profiles. There were indications, however, that vegetation accumulated Cd preferentially to Pb.

In 1973, an investigation was conducted to determine if heavy metals were indeed a threat to organisms living near a highway. Gish and Christensen (12) studied the accumulation of Cd, Ni, Pb, and Zn in earthworms from roadside soil. They found that earthworms accumulated up to 331.4 ppm Pb, 670 ppm Zn, 37.5 ppm Ni, and 14.4 ppm Cd at a distance of 3 m from the highway. Cd, Ni, Pb, and Zn concentrations in earthworms averaged 11.2, 5.7, 1.9, and 0.95 times that of the surrounding soil. The authors felt that the Pb and Zn levels in earthworms were high enough that other animals feeding on the earthworms for an extended period of time could acquire toxic levels of these metals in their bodies.

Nightengale (13) sampled soil from urban runoff retention basins and found accumulations of Pb, Zn, and Cu in the top 5 cm of soil with lesser amounts found deeper in the soil. Within the first 5 cm of soil, the arithmetic mean concentrations of Pb, Zn, and Cu were 224.8, 107.9, and 19.9 mg/Kg, respectively. Newton et al. (14) sampled snow adjacent to a heavily traveled street and found an average Pb concentration to be 5.5 mg/l. Pb concentration in samples farther away from the roadbed decreased with increasing distance. The authors noted that volume of traffic, type of traffic, and speed of vehicles could affect the Pb concentration found.

Helsel et al. (15) found good, non-linear correlations between Pb, Zn, and Cu with traffic and percent impervious cover. The authors felt that these individual land use characteristics were better indications of stormwater quality than broad land use types such as commercial, agricultural, etc. Moreover, the authors felt that close correlations point towards motor vehicles being the major source for Pb, Zn, and Cu present in urban runoff.

Recognizing the presence of heavy metals on street surfaces and highways in urban areas, many studies have been conducted to determine the concentrations of these metals in urban stormwater and runoff. Table 2 summarizes the results of several studies. Colston (10), in his Durham, N.C. study, noted that the contribution of heavy metals from urban runoff was approximately two and one-half times as great as typical raw wastewater. In the Lodi, N.J. study (16), the authors noted that Pb, Zn, and Cu accounted for approximately 90 to 98 percent of the metals observed. Moreover, Pb, Cu, and Zn accounted for approximately 84 percent of the total contribution of metals from urban stormwater. It was also estimated that 86 percent of the total annual load of metals came from urban stormwater. In the Virginia study (17), heavy metals were concluded to be one of the most significant parameters

Table 2

Heavy Metal Concentrations in Urban Runoff (mg/l)

Location and Date	Land Use	Pb	Zn	Cu	Cr	Ni	Reference
Durham, N.C. 1970	Residential	0.45	0.36	0.15	0.23	0.15	10
Lodi, N.J. 1975	Urban/ Residential	0.90	0.62	0.15	0.03	0.08	16
Virginia 1975	Residential	0.35	0.13	0.06	0.06	0.02	17
	Commercial	0.45	0.49	0.07	0.04	0.07	17

of urban runoff together with suspended solids and organic matter. Table 3 presents estimated loadings of heavy metals from urban runoff for these studies.

The potential impact heavy metals from urban runoff have upon a stream is very great. In a hypothetical case study of potential water quality problems associated with urban runoff, Pitt and Field (18) found that toxic heavy metals had a large impact upon a receiving stream. To protect the receiving stream from the most restrictive use (propagation of fish), it was estimated that Fe, Pb, Zn, and Cu would have to be reduced 99, 94, 97, and 80 percent, respectively.

Heavy Metals in Streams and Rivers

Livingston (19) reviewed the literature that reported metal concentrations in streams and rivers around the world and presented the following global mean concentrations for Cu, Ni, and Zn, 10 ppb; and ranges for Pb, 1-10 ppb; and Cr, 0.1-10 ppb. Andelman (20) presented data accumulated by Kopp and Kroner (21) showing the variability of heavy metals encountered for river basins in three regions of the U.S. Zinc concentration in all rivers of the United States averaged 64 μg/l, while concentrations of 96, 205, and 28 μg/l were found in the Northeast, Lake Erie, and Alaskan regions. Similarly, Cu, Ni, and Pb concentrations for all the United States were found to be 15, 19, and 23 μg/l, respectively. These metal concentrations averaged, respectively, 15, 11, and 9 μg/l for the Northeast region; 11, 5, and 39 μg/l for the Lake Erie region; and 9, 5, and 12 μg/l for the Alaskan region.

Table 3

Estimated Annual Contributions of Heavy Metals From Urban Runoff

Location	Land Use	Pb	Zn	Cu	Cr	Ni	Reference
Durham, N.C. (lb/sq. mi./yr)	Residential	1,856	1,280	1,024	1,024	768	10
Lodi, N.J. (lb/yr)	Urban/ Residential	11,697	8,058	1,950	389	1,039	16
Virginia	Residential	1,533	794	305	75	155	17
(lb/sq. mi./yr)	Commercial	4,198	2,190	3,103	365	1,223	17

Turekian and Scott (22) also found that regional differences existed for concentrations of Cr, Ag, Mo, Ni, Co, and Mn in suspended material in streams. The Mississippi River and Central U.S. rivers were found to have higher suspended loads rich in montmorillonite (a clay), whereas western rivers contained more organic carbon, and eastern rivers contained lower suspended loads. However, the eastern U.S. streams were found to contain higher concentrations of most elements than the western U.S. streams.

The presence of certain heavy metals in a stream or river can often indicate the type of geography and land use the stream or river flows through. For example, Williams et al. (23) presented various metal concentrations reflecting four different regions through which the Hudson River flows. The authors noted that dissolved Fe and Mn concentrations of 89.5 and 2.5 μg/l were higher in the precambrian coniferous regions than those regions consisting of glacial till and sedimentary rocks. Upstream Cu and Zn concentrations of 3.2 and 4.3 μg/l, respectively, increased to 7.1 and 9.3 μg/l, respectively, reflecting small quantities of municipal and industrial waste discharges downstream. These concentrations for Cu and Zn increased to 11.0 and 57.0 μg/l, respectively, further downstream as larger quantities of industrial wastes were discharged into the river. Additionally, dissolved Cr concentrations increased from 0-3 μg/l upstream to 6.0 μg/l downstream near the regions of larger industrial discharges. Iron concentrations, however, decreased to 58 μg/l while Mn concentration essentially remained unchanged at 2.1 μg/l as the river progressed downstream.

In a study conducted by Kubota and Mills (24), twelve streams--four of which flowed through the urbanized center of Ithaca, New York--were selected to determine the concentration of Pb, Cd, Zn, and Cu. It was found that suspended particulates of the streams flowing through the urbanized area contained approximately 50 percent more Zn, 85 percent more Cu, and 100 percent more Co than those flowing through rural areas. All four urbanized streams had consistently higher Pb concentrations in the particulate fraction than the rural streams. No significant difference, however, existed between the urban and rural streams for the soluble metal fraction. Mean concentrations of soluble Pb, Cd, Zn, Cu, and Co in the four urbanized streams, respectively, were 0.8, 0.2, 2.4, 1.0, and 0.05 μg/l, and 0.8, 0.3, 2.6, 0.5, and 0.04 μg/l in the rural streams. Mean particulate Pb, Cd, Zn, Cu, and Co concentrations in urbanized streams were 3.5, 0.2, 12.1, 3.1, and 0.15 μg/l, respectively, while in rural streams the concentrations were 1.3, 0.09, 7.0, 1.7, and 0.09 μg/l, respectively.

To evaluate the possible sources of the trace particulate metals found in the streams, soils of the surrounding area were also analyzed for the metals in question. It was found that the mean concentrations of Pb and Cd in suspended particulates was appreciably greater than the surrounding soils. Cu and Zn concentrations were somewhat greater while Co concentrations were about the same. Moreover, maximum Pb, Zn, Cd, and Co concentrations were found in early spring, suggesting to the authors that sources other than the soils accounted for the amounts found. The authors noted that heavy metals in particulates from streams of an urban area may represent many diverse inputs such as industrial, automotive, and domestic uses.

Gale _et al_. (25) found that finely divided particulate matter bearing Pb, Zn, and Cu contribute to the pollutional load of a stream in Missouri's new lead belt. The particles derived from mining and milling operations were especially noticeable during periods of storm runoff. Pb, Zn, and Cu concentrations existing in the dissolved state were usually very low. Unfiltered samples of Pb, Zn, Cd, Cu, and Mn from an upstream control station were 0.011, 0.010, <0.010, <0.010 µg/l, respectively. Unfiltered samples from three downstream stations contained 0.035, 0.033, and 0.030 µg/l Pb; 0.140, 0.134, and 0.038 µg/l Zn; <0.010, <0.010, and <0.010 µg/l Cd; 0.017, 0.012, and <0.010 µg/l Cu; and 1.637, 1.691, and 0.480 µg/l Mn.

Weiss _et al_. (26) also found that the suspended fraction for the metals Cr, Hg, Pb, and Zn were greater than the dissolved fraction for these metals. Cd values, however, were too erratic to draw any conclusion. Mean total metal concentrations (ppb) from control streams of the Haw River were: Cd, 0.7; Cr, 2.3; Hg, 0.05; Pb, 1.1; and Zn, 6.8. Mean total metal concentrations (ppb) from the main stem of the Haw River which flows through an urbanized area were: Cd, 0.7; Cr, 3.4; Hg, 0.08; Pb, 3.8; and Zn, 6.6.

Degroot _et al_. (27) also found that in addition to their natural content of heavy metals, rivers carry large amounts of heavy metals sorbed onto the suspended sediment from pollutional sources. Pb, Cr, Cu, As, and Hg were generally carried by the suspended load. Zn and Ni, however, were generally transported in the soluble form.

Heavy metals in water can be transported in the dissolved, colloidal, or particulate phase. Perhac (28), in studying the distribution of Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn from two streams in Tennessee, found that over 90 percent of each metal occurred in the dissolved solids, less than 10 percent occurred in the coarse particulate solids, and less than 1 percent occurred in the colloidal solids. However, the highest concentration (ppm metal in the solid fraction) occurred in the colloids while the lowest concentration occurred in the dissolved state. Although the metals were most concentrated in the colloids, the greatest quantity of metal occurred in the dissolved solid because the dissolved solids comprised most of the total solids present in the water.

Gibbs (29) proposed that heavy metals are transported in water by five following mechanisms: (1) crystalline particles, (2) metal hydroxides, (3) solid organic matter, (4) sorbed material, and (5) metals in solution. For the Amazon and Yukon Rivers, Gibbs found that Cu and Cr were mainly transported in the crystalline solid, Mn in the hydroxide coatings, while Fe, Ni, and Co were equally transported by both mechanisms. Percentages of the total amounts of Fe, Ni, Co, Cr, Cu, and Mn transported by the five aforementioned mechanisms were: (1) 48.2, 31.0, 51.4, 64.5, 87.3, and 37.1; (2) 40.6, 47.8, 29.2, 7.2, 3.8, and 45.7; (3) 11.0, 16.0, 12.9, 13.2, 3.3, and 6.6; (4) 0.01, 3.1, 4.7, 2.3, 2.3, and 0.5; (5) 0.05, 2.2, 1.7, 12.6, 3.3, and 10.1. In a subsequent article (30), Gibbs concluded that the major transport mechanisms for Cr, Mn, Fe, Co, Ni, and Cu in the Amazon and Yukon Rivers were crystalline particles and hydroxide coatings on particles that accounted for between 65 and 92 percent of the total metals transported.

Angino's work (31) corroborated Gibbs' findings that co-precipitation in metallic coatings is indeed a major transport mechanism for heavy metals in water. Significant correlations of Ni, Pb, Zn, with Fe and Mn on suspended sediment were strongly suggestive of co-precipitation of these metals with Fe- and Mn- oxide coatings. The author also presented data suggesting that no relation existed between Fe, Ni, Zn, and Pb concentrations in solution with the concentrations in the suspended sediment. Additionally the author found no relation between soluble or suspended metal concentration with discharge.

This finding, however, was not in agreement with the findings of Williams _et al_. (32). Although no correlations were found to exist between stream flow and soluble heavy metal concentrations in the Williams _et al_. investigation, a strong positive correlation was found between total heavy metals and increased stream flow. Suspended Cu, Fe, Mn, Hg, and Zn concentrations associated with sediments were thought to increase due to resuspension into the water column following bottom scours that resulted from increased stream velocities.

Heavy Metals in Sediments

The existence and relative concentrations of trace metals in stream and lake sediments reflect both the natural geological background and man-induced anthrogenic inputs. Steele and Wagner (33) found that the metal content of the sediment reflected the geology through which the Buffalo River in Arkansas flows. Na and K concentrations in sediment were found to be greater upstream, reflecting the shale environment. Also, Fe and Fe- associated elements (Co, Ni, Cr, Mn) were found to be in higher concentrations upstream. Downstream, as the river flowed through more limestone and dolomite than shale, concentrations of Mg and Ca increased. As the river flowed through intense mining areas, Pb, Zn, and Cd, concentrations were found to increase.

Many studies have shown abnormally high metal concentrations in sediments from areas receiving various types of pollutional inputs compared to metal concentrations in sediments taken from natural geological areas. Richert *et al*. (34) noted that if trace elements in the Willamette River represented only natural or unpolluted conditions, the concentrations would be expected to follow either a normal or log normal distribution. Therefore, probability plots for the metals under consideration were developed for the length of the Willamette River. Plots for Zn, Pb, Cu, and Cr concentrations all displayed a curve distinguished by the formation of two district segments where each segment represented data from either polluted or unpolluted locations.

Zn concentrations, when plotted on normal probability paper, defined one segment of the curve in which samples collected above a pulpmill showed lower concentrations than samples collected downstream of the pulpmill. Pb concentrations, similarly plotted, defined one segment of the curve in which samples collected at discrete locations receiving stormwater from urbanized areas showed higher concentrations than samples collected from unurbanized areas. Cu concentrations, similarly plotted, also showed higher concentrations in the areas where high Zn and Pb concentrations were found than those found in the backwood areas.

Pezzetta and Iskandar (35), in studying the sediments in Green Bay, Wisconsin, found that the levels of Cr, Cu, Zn, and Cd were from two to four times greater in the recent sediments than in the underlying glaciolacustrine deposits of red clay. The authors suggested that industrial and municipal wastes, erosion, runoff from agricultural and urban lands, and atmospheric fallout may be the source of the Cr, Cu, and Zn. Additionally, the heavy metals were found to be more concentrated in the fine-grained sediments of the river and shipping channel than the coarser fraction along the river banks. Cu concentrations, for instance, varied from 1 μg/g to 92 μg/g in the shipping channel. Zn concentrations ranged from 7 μg/g to 204 μg/g. Varying Cu and Zn concentrations were also found adjacent to a power plant discharge.

Maxfield *et al*. (36) found low concentrations of Pb, Zn, Cd, and Cu in the St. Joe River, which is relatively free of urban, rural, and mining pollution, but higher concentrations in the Coeur D'Alene River which drains urban and mining areas. Pb, Zn, Cu, and Cd concentrations were found to decrease from 3200, 5000, 110, and 90 ppm, respectively, in the Coeur D'Alene River to 100, 100, 20, and 10 ppm, respectively, in the St. Joe River.

Mathis and Cummings (37) also found that metal concentrations in sediments of the industrial-use Illinois River were significantly higher than three non-industrial-use streams. Concentrations of Cu, Ni, Pb, Cr, Zn, and Cd were 23, 11, 17, 10, 41, and 1.1 ppm, respectively, in the Illinois River sediments. Cu concentration in the Illinois River sediments were 2.5 times greater than in those streams not associated with industries. Similarly, concentrations of Ni, Pb, Cr, Zn, and Cd were, respectively, 1.7, 1.6, 2.8, 2.7, and 5.0 times higher.

The retention of heavy metals on sediment particles has been attributed to a variety of control mechanisms. The Fe_2O_3 films surrounding sediment particles have been pointed to as one mechanism for capturing and retaining many heavy metals from the overlying water column. Jenne (38) believes that the hydrous oxides of Mn and Fe furnish a principal control mechanism for the fixation of Co, Cu, and Zn in soils, clays, and sediments. Steele and Wagner (33) also found that Co, Mn, Cr, and Ni were retained in the Fe_2O_3 films solely and were not carried by clastic grains. Mg, Ca, Zn, Cd, Cu, and Pb, however, existed and were transported in clasts as well as in the oxide coatings surrounding sediment particles. As discussed previously, other investigators (29, 30, 31) also noted the distinct possibility of the metals Ni, Pb, and Zn being co-precipitated with Fe and other oxides on suspended sediments.

The presence of organic carbon has also been postulated as a control mechanism for the retention of heavy metals in sediments. Shimp et al. (39) found it reasonable to assume that soluble or colloidal organo-metallic complexes play an important role in the transport and sedimentation of trace elements in Lake Michigan. Pb, Zn, and Cr concentrations in sediment were found to be correlated with the amount of organic carbon present at varying depths.

Loring (40) found that organic matter appeared to be the major source of the non-detrital (acid soluble) fraction of heavy metals in sediments. Trace metal accumulation was also found to be related to the deposition of fine-grained inorganic and organic matter. Moreover, the amount of acid-soluble Zn, Cu, and Pb associated with organic carbon was found to be directly related to C/N ratios in the order Pb > Zn > Cu. Iskandar and Keeney (41), on the other hand, found no consistent relationship between organic carbon and heavy metals in their investigation of sediments in selected Wisconsin lakes.

Relative sediment particle size is another important consideration when analyzing sediments for heavy metals. Oliver (42) found that fine-grained sediment samples generally contained more heavy metals than coarser grained samples. The average metal concentrations (in ppm) for a silt sample was: Pb, 33; Hg, 0.22; Zn, 88; Cu, 25; and Cr, 2.7; whereas the average metal concentrations (in ppm) for a medium grain size sample were: Pb, 5; Hg, 0.15; Zn, 4; Cu, 9; Ni, 10; Co, 6; Fe, 4,300; Mn, 63; and Cr, 9. Oliver concluded that the difference in metal concentrations for sediments with different grain-size distributions is so great it is important to consider difference in particle size when comparing two sediment samples from two different locations.

Rickert (34) found that sediments containing different proportions of material less than 20 μ could largely determine the measured concentration of Cu, Pb, and Zn. Using 44 samples, the ratios of average metal concentrations in material less than 20 μ (clay plus silt) to material less than 2 mm (combined clay, silt, and sand) were: Cu, 4.3; Pb, 2.4; Zn, 1.8; Hg, 1.2; and Cr, 0.8. Thus, sample surface area, as represented by the weight percentage of <20 μ material, was an important control on the measured concentrations of Cu, Pb, and Zn, but an insignficant control on the measured concentrations of Hg and Cr.

Pita and Hyne (43) suggested that heavy metals transported in the suspended load could be adsorbed onto clay mineral surfaces and deposited in the sediment. Because the investigators found that most of the Zn and Pb occurred in the 2.0-2.9 specific gravity portions, they believed that Zn and Pb were deposited as zwitterions or organometallic complexes adhering to clay surfaces. Pezzetta and Iskandar (35) also found correlations with heavy metal and particle size but, in their study, silt-size particles seemed to act as a better control mechanism than clay-size particles.

Another possible control mechanism for retaining heavy metals in sediments is that of co-precipitation with the sulfide ion. Holmes _et al_. (44) proposed that Zn and Cd in a marine estuarine system were precipitated as ZnS and CdS when anoxic and reducing conditions were present. Loring (40) also presented data indicating that most of the Zn, Cu, and Pb found in the detrital (acid-soluble) fraction was held by discrete sulfide minerals.

Heavy Metals in Aquatic Organisms

Heavy metals present in water can be found either in high enough concentrations to be toxic to aquatic organisms or low enough concentrations to be accumulated by the organisms and thus be removed from the water. Warnick and Bell (45) determined the toxicity of Cu, Zn, Cd, Pb, Fe, Ni, Co, Cr, and Hg salts to three species of aquatic insects. The investigators found that the mayfly _Ephemerella_ was the most sensitive to all metals studied. Hg was found to be toxic to the stonefly _Acroneuria_ at 33.5 mg/l and Co to the caddisfly _Hydropsyche_ at 64.0 mg/l. In all other cases, the test organisms lived byond 96 hours even at concentrations up to 64.0 mg/l indicating that aquatic organisms were not as sensitive to heavy metals as fish.

Rehwoldt _et al_. (46) investigated the effects of heavy metals upon the aquatic environment of the Hudson River. For an unidentified caddisfly (Trichoptera) the 24- and 96-hour LC_{50} were, respectively, 12.1 and 6.2 mg/l for Cu^{++}; 62.6 and 58.1 mg/l for Zn^{++}; 48.4 and 30.2 mg/l for Ni^{++}; 5.1 and 3.4 mg/l for Cd^{++}; 5.6 and 1.2 mg/l for

Hg^{++}; and 58 and 50 mg/l for Cr^{++}. For snails (Amnicola sp.), the 24- and 96-hour LC_{50} were, respectively, 1.5 and 0.9 mg/l for Cu^{++}; 16.8 and 14.0 mg/l for Zn^{++}; 21.2 and 14.3 mg/l for Ni^{++}; 10.1 and 8.4 mg/l for Cd^{++}; 1.1 and 0.08 mg/l for Hg^{++}; and 10.2 and 8.4 mg/l for Cr^{++}.

Nehring (47) found that the 14-day TL_{50} for a mayfly ranged from 0.8 to 0.20 mg/l for Cu, 3.5 mg/l for Pb, was less than 0.001 mg/l for Ag, and was greater than 9.2 mg/l for Zn. For a stonefly, the 14-day TL_{50} values ranged from 10.1 to 13.9 mg/l for Cu and 0.004 to 0.009 mg/l for Ag, and was greater than 19.2 mg/l for Pb and 13.9 mg/l for Zn. Nehring also concluded that the aquatic insects seemed to be more tolerant of all heavy metals tested than fish with the exception of silver for the mayfly.

If the metals present are in amounts less than the toxic level for a given organism, then the metals may be bioconcentrated by that organism. Kneip and Lauer (48) referred to bioconcentration (concentration factor) as the ability of an organism or a population of many organisms of the same trophic level to concentrate a substance from an aquatic system. Two general processes that may be involved in the uptake of trace elements by organisms in the aquatic environment are the transfer of ionic species or dissolved substances by the organism, and the ingestion of particulate matter by the organism (49). If the organism continues to concentrate the substance throughout its active metabolic lifetime such that the concentration factor, if calculated, would be continuously increasing, then bioaccumulation is said to occur (48).

Many studies have noted the phenomenon of bioconcentration. Pringle *et al*. (50) found that mollusks in a natural estuarine environment accumulated trace metals at different rates and attained tissue levels higher than environmental levels depending upon the particular metal and species, the temperature, salinity, and dissolved oxygen, and the physiological activity of the organism itself. For example, different specimens were found to concentrate different metals at various concentrations and rates. For the soft-shell clam (*Mya arenaria*), Cu, Zn, Cd, and Pb were respectively concentrated at rates of 3, 0.35, 0.16, and 3.0 ppm per kg per day. However, uptake rates and tissue concentrations decreased for the other two species investigated. It was also noted that by doubling the exposure level of Pb resulted in twice the rate of uptake for that metal. Furthermore, temperature, salinity, dissolved oxygen, pumping rates, and physiological conditions of the animal were all closely related to the uptake and concentration level attained for any given metal for all specimens studied. Additionally, each metal accumulated more in certain anatomical areas than the other metals. Highest Pb concentrations in the eastern oyster (*Crossotrea Virginica*), for instance, were found to accumulate in the digestive glands and gonads, whereas lowest Pb concentrations were found to accumulate in the muscle and the mantle.

Many studies have linked high metal concentrations in aquatic organisms to man-induced pollutional sources. Stenner and Nickless (51) found abnormally high Cd and Pb concentrations, and higher than normal Zn concentrations in marine organisms near the sites of metal smelters in Hardangerfjord, Norway. Wharfe and Van Den Broch (52) found that Pb and Cd concentrations in mussels, shore crabs, and periwinkles were higher in industrialized areas. Huggett *et al*. (53) also found that concentrations of Cd, Cu, and Zn in eastern oytsters were functions of the source of pollutants and the animal's position in an estuary.

DiGiano *et al*. (54), in their study of the impact of urban runoff upon a receiving stream, found very high concentrations of Cu and Pb in snails and leeches downstream of the runoff input. Although common organisms could not be found both upstream and downstream, no Pb was found in benthic organisms upstream. However, Pb concentrations for the two types of snail found downstream were 136 and 40 ppm and 40 ppm for leeches.

Because of aquatic organisms ability to concentrate heavy metals, Nehring (47) suggested that specific aquatic insects could be used as biological monitors of heavy metal pollution. Nehring found that a constant relationship existed with the exposure level of a heavy metal concentration in the water and the heavy metal concentration accumulated by the aquatic insect. This constant relationship is the concentration factor, defined as the ratio of the average level of metal exposure in the water to the average level of metal accumulation in the aquatic insect. The concentration factor for Cu in a stonefly, for instance, ranged from 185 to 217. For all metals studied, the concentration factor estimated the actual level of exposure with an accuracy of 80 percent or better for 19 out of 28 trials and 90 percent or better for 10 out of 28 trials.

In an extensive study carried out by Weiss et al. (26) in North Carolina, heavy metal concentrations in aquatic insects for a control stream and industrial-use stream were determined. It was found that in the main stem of the Haw River, average Cd, Cr, Hg, Pb, and Zn concentrations for all orders of aquatic insects studied were 1.8, 111, 5.5, 23.2, and 3.57 ppm, respectively. Metal concentrations found in the control stream were 2.0, 13.8, 8.1, 5.9, and 241 ppm, respectively.

Generally, metal concentrations for all macroinvertebrates followed the sequence Cd < Pb = Hg < Cr < Zn. When concentrations of Cr were higher than Zn in the water, Zn concentrations were still higher than Cr concentrations in organisms. However, where average Cr concentrations in water were relatively high, average Cr concentrations in organisms were also relatively high, indicating a relation between Cr concentration in water and organisms. Also, the highest concentrations of all metals in organisms were found to occur in summer and early fall. Additionally, no one organism consistently concentrated any of the metals studied to a greater degree than any other organism. However, a trend did exist suggesting the order of affinity for Pb and Zn in organisms was Odonata < Trichoptera < Ephemeroptera. Generally, Ephemeroptera concentrated more Cr than either Odonata or Trichoptera. Cd, however, did not demonstrate a strict affinity for any particular order of aquatic insect.

If metals are concentrated by organisms of lower trophic levels, the possibility of biomagnification occurring may exist. Kneip and Lauer (48) use the term biomagnification when a substance is found to exist at successively higher concentrations with increasing trophic levels in an ecosystem's food chain. Presenting data first published by Ljunggren (55), Kneip and Lauer (48) pointed out that bioconcentration may exist for a substance in many trophic levels reflecting different upstream and downstream conditions, but biomagnification need not occur if organisms of higher trophic levels concentrate the substance less than organisms of lower trophic levels. In the study by Ljunggren (58), downstream plants, plankton, crustacea, aquatic insects, and fish contained Cd concentrations, respectively, of 20,000, 7,000, 6,000, 10,000, and 2,000 mg/g; while upstream Cd concentrations were 2,000, 800, 1,000, 6,000, and 500 mg/g, respectively. Thus, bioconcentration occurred without subsequent biomagnification occurring.

Metal concentration of various organisms at different trophic levels is often dependent upon the feeding habits of each individual organism. Phelps (56) studied the partitioning of elements within a benthic community and found that the qualitative and quantitative structure of the community had a direct effect upon the distribution of elements throughout the community. Metal concentrations were highest for those organisms most dependent on sediment such as the select deposit feeders, polychaetes, that fed on recently settled particular matter. On the other hand, metal concentrations were lowest for those non-select deposit feeders, such as omnivores and carnivores, that fed on sediments, detritus, and other living organisms. Thus, feeding habits may dictate relative metal concentrations among a group of organisms.

Mathis and Cummings (37) found that concentrations of metals in bottom-dwelling tubificid worms and clams closely reflected the concentration of metals found in the bottom sediments of the Illinois River. However, with the exception of Cu in worms, metals were more highly concentrated in the sediments. Moreover, biomagnification was not found to occur. A concentration gradient ranging from highest levels in worms, intermediate levels in clams, and lowest levels in fish fillets was found to occur for Cu, Ni, Pb, Cr, Li, Co, and Cd. Zn, however, showed a partial reversal of this trend. Although metal concentrations in fish were higher than levels in surrounding water suggesting bioconcentration, biomagnification did not occur since metal concentrations in omnivorous fish were about the same as carnivorous fish and since metals did not concentrate along successively higher trophic levels.

Gale *et al*. (25) also found that Pb, Zn, Cu, and Mn originating from lead mines were not concentrated through successively higher trophic levels. Small concentration factors did exist for the consumer organisms such as crayfish and minnows, but not to any appreciable extent. Pb, Zn, Cu, and Mn concentrations in aquatic vegetation, however, were found to be inversely related to distance downstream of tailings ponds. Concentrations of Pb and Zn in a pond weed (*Potamogeton*) were found to be 7,000 and 5,000 ppm, respectively, in the tailings ponds and 250 ppm for both metals approximately two miles downstream. Similarly, Pb and Zn concentrations in snails were found to be 116 and 54 ppm, respectively, 0.2 miles below a tailings pond and 44 and 18 ppm, respectively, 2.8 miles below the pond. Distance downstream and heavy metal concentration relationships in crayfish, tadpoles, and minnows were not as consistent as those for aquatic plants and snails, but evidence of a small trend did exist.

In another study by Hutchinson et al. (57), high concentration factors based upon Ni and Cu concentrations in water for aquatic organisms were found but, again, biomagnification was not found to occur. Water, sediments, periphyton, pelagic zooplankton, photoplankton, and benthic organisms were sampled from a number of bays and rivers receiving various degrees of pollutional inputs from Ni and Cu smelters around the Sudley region in Canada. Ni and Cu levels in the water varied according to input source. Additionally, metal concentrations in water correlated well with metal concentrations in sediment, periphyton, zooplankton, crayfish, and clams, suggesting that bioconcentration had occurred. For example, average Ni concentrations in water, sediment, Potamogeton sp., periphyton, zooplankton, crayfish, and clams from the Wanapitei River were 42 ppb, 224 ppm, 193 ppm, 480 ppm, 826 ppm, 27 ppm, and 39 ppm, respectively, whereas Ni concentrations from the Pickerel River were 2 ppb, 13 ppm, 39 ppm, 43 ppm, 7 ppm, blank, and 4 ppm, respectively. Highest concentrations of Ni were found in algal periphyton, whereas highest concentrations of Cu were found in crayfish because of its cyanoglobin system.

The relative ratios of Ni to Cu in the water and sediments were generally maintained in plants, but the animals exercised remarkable selectivity in metal uptake and excretion that dramatically changed the ratios. Again, concentration factors for organisms at higher trophic levels were considerably lower than those organisms of lower trophic levels. Concentration factors for Ni and Cu, respectively, were 5,333 and 12,222 for sediment; 11,429 and 9,000 for Potomageton sp.; 19,667 and 17,667 for periphyton; 643 and 3,444 for zooplankton; 262 and 2,222 for clams; 929 and 3,911 for crayfish; 226 and 149 for omnivorous fish; and 329 and 156 for carnivorous fish. The very large differences between organisms were thought to be caused from differences in feeding habits. Furthermore, while very large concentration factors existed for many parts of the ecosystem, biomagnification through the food chain did not occur.

III. MATERIALS AND METHODS

Description and Location of Sampling Stations

Bull Run, which flows from a primarily agricultural area through the progressively urbanized areas of Manassas Park and Manassas in northern Virginia, was selected as the stream of study (Fig. 1). There are few, if any, industrial discharges that may contribute heavy metals into Bull Run. Sewage treatment plants, however, do enter Bull Run by way of direct discharge from Greater Manassas Sewage District plant (GMSD) and from those contributed by two tributaries, Cub Run and Flat Branch. Thus, the major sources of heavy metals into Bull Run are urban runoff and stormwater discharges.

Although both Cub Run and Flat Branch carried sewage effluents into Bull Run at the time of this study, each stream drains significantly different land use areas. Cub Run drains predominantly agricultural areas in Loudoun and Fairfax Counties. However, it does cross Route 66 which could serve as a source for heavy metals into Bull Run. In contrast, Flat Branch drains most of the Manassas Park area, which includes residential, commercial, and a small amount of industrial land-use categories. Thus, the major source for heavy metals originating from urban runoff to Bull Run was that from Flat Branch.

Therefore, suspected sources of urban runoff became a major consideration in the selection of sampling locations. Attempts were made to choose locations that received inputs from increasingly urbanized areas beginning with an upstream control station situated in a primarily

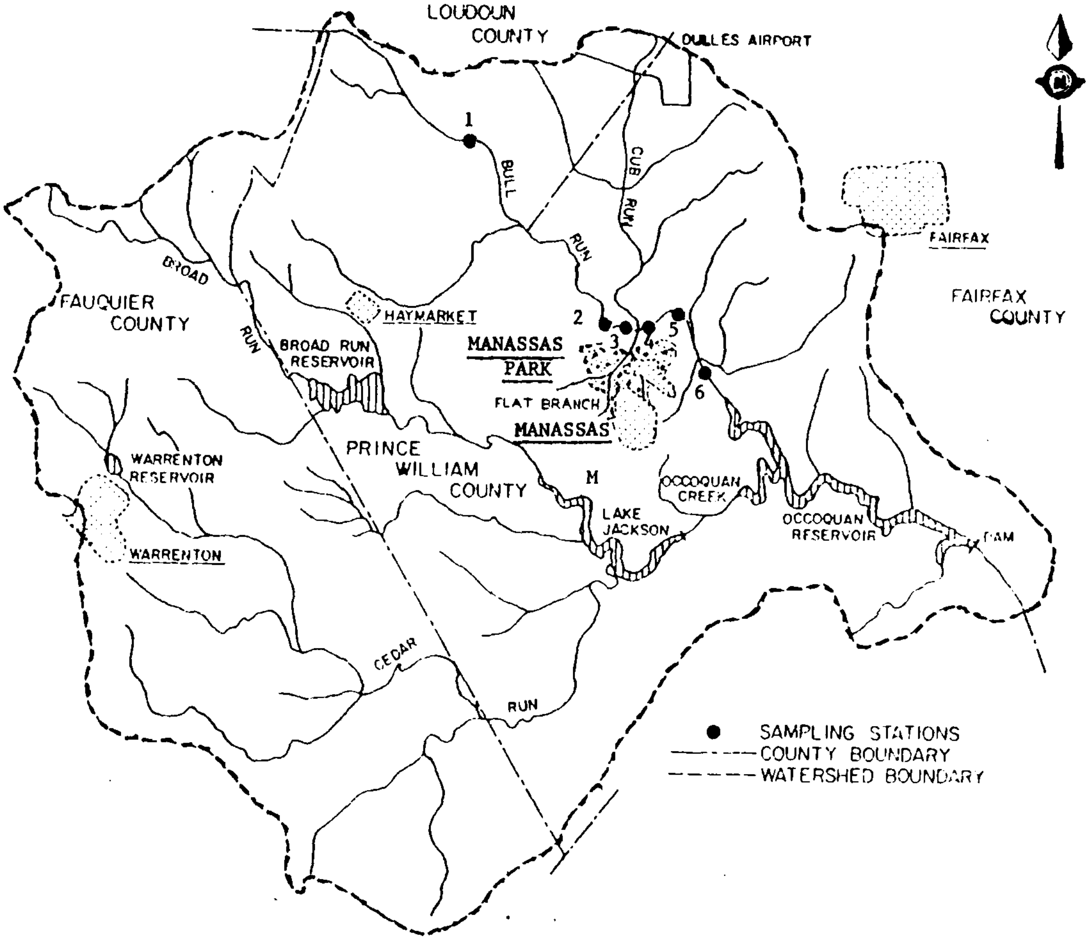


Figure 1. Map of Study Area

agricultural area, continuing with stations located in the urbanized areas of Manassas Park and Manassas, and ending with a downstream station considerably removed from direct urban runoff inputs. Consideration was also given to the ecological similarity and physical nature of the stations, both of which are important when seeking organisms common to each station.

Six sampling stations were located along Bull Run (Figure 1). Three of these were located upstream of Flat Branch, which is believed to be the major source of urban stormwater input into Bull Run. These three stations included the upstream control station at Catharpin (Station 1), the Bull Run Regional Park station located downstream of Route 66 (Station 2), and the Ben Lomond Park station located just upstream of Flat Branch (Station 3). Three more stations were located downstream of Flat Branch in order to determine the tributary's effect upon Bull Run. These three stations included the Bull Run Trailer Park station located just downstream of Flat Branch (Station 4), the Yorkshire station located some distance downstream of GMSD (Station 5), and the downstream station at Yates Ford (Station 6). Table 4 gives locations, site descriptions, and other pertinent information for each stream station.

Sampling Procedures

Due to the number of stations and the long distances between them, sampling the total study area required two days. Physical, chemical, and hydrologic measurements (pH, temperature, dissolved oxygen (D.O.), hardness, alkalinity, gage height) were taken on the first

Table 4

Description and Location of the Bull Run Stream Stations

Stream Station	Location*	Downstream Distance from Station 1 (km)	Site Description
1	Catharpin	--	This control station drained primarily pasture and agricultural areas and was located well upstream of any urban runoff inputs. The bottom substrate (3-6 in. flat rocks) supported a large benthic community. The actual sampling point was a riffle and was located 50 m downstream of a USGS gaging station on Route 705.
2	Bull Run Regional Park	18.7	Station 2 received urban runoff from Route 66 (1.6 mm upstream). The bottom substrate (rock bottom) supported a large population of attached algae and benthos. Samples were collected along a riffle.
3	Ben Lomond Park	21.1	Station 3 was located 0.2 km upstream of Flat Branch and received some drainage from the surrounding residential area. The bottom was silty and unable to provide a suitable habitat for a diverse benthic community. Samples were collected where the average stream depth was 30 to 40 cm.

Table 4 (Continued)

Stream Station	Location*	Downstream Distance from Station 1 (km)	Site Description
4	Bull Run Trailer Park	22.1	Station 4 was located immediately downstream (0.7 km) of the stormwater carried by Flat Branch from Manassas and Manassas Park. Cub Run and another unnamed wet-weather stream joined Bull Run upstream of this station. Samples were collected on a riffle where the bottom substrate (rocky bottom) supported a large benthic community. A USGS gaging station (0.67 km downstream) on Route 616 was used for flow data.
5	Yorkshire	25.7	Station 5 was located on Yorkshire along the property of Mr. and Mrs. Richard Bragg and received urban drainage from this development and Route 28 (1.8 km upstream). The bottom was composed of gravel and fine sand and was unable to provide a suitable habitat for a diverse benthic community. Samples were collected where the average stream depth was 20-30 cm.
6	Yates Ford	30.5	Station 6 received drainage from Manassas and Manassas Park and other areas from many small tributaries. The bottom substrate (large rocks and railroad ties) supported a large population of attached algae and benthos. Samples were collected along the riffle caused by the railroad ties. A USGS gaging station, at this point, was used for flow data.

*See Figure 1.

day. Water samples for metals, total organic carbon (TOC), and solids analyses were also collected at this time. The following day, sediment, detritus, and biological samples were taken. Eight hours were required to complete one day's sampling.

At each station, pH, temperature, D.O., alkalinity, and hardness were measured on-site and samples of water, sediment, detritus, and crayfish were collected. Because of different ecological characteristics among the six stations, all stations did not support a viable benthic community. Caddisfly larvae (Hydropsychidae) were collected at Stations 1, 2, 4, and 6. It was also possible to collect the snail Pleuocera sp. at Stations 2 and 6. Gage heights for determining flow rates were recorded from the existing USGS gaging station at Stations 1, 4, and 6.

Water samples for metal analyses were collected in acid-washed, polyethylene containers. Those samples to be analyzed for total metals were acidified with 1:1 nitric acid (HNO_3) to a pH less than 2. However, those samples to be analyzed for dissolved (filterable) metals were not acidified upon collection, but were cooled to 4°C and filtered through an acid-washed, glass-fiber filter. (All filtrations used for metal analyses were performed using acid-washed glass-fiber filters and receiving flasks.) The sample was then acidified with 1:1 HNO_3 to a pH less than 2. Water samples collected for TOC were also acidified to a pH less than 2 with 1:1 HNO_3. Samples collected for solids determination were stored at 4°C prior to analysis.

Sediment samples were collected by using a polyethylene beaker to remove approximately the top 6 cm of sediment. These samples were collected at specific locations at each station from a pool or where some other stilling effect allowed sufficient sediment to accumulate. The sample was then sieved through a 10 mesh (2 mm) polyethylene sieve to remove large rocks and detritus, and left to air dry for approximately 30 minutes. The sieved sediment was then put into a plastic bag and immediately frozen with dry ice to prevent any microbial activity.

Snails, caddisflies, and crayfish were collected with a D-framed kicknet. Sufficient quantities of each organism were picked out, placed in an acid-washed polyethylene container, and frozen with dry ice. Detritus samples were collected with the biological samples, separated from the organisms, put into a plastic bag, and, likewise, frozen with dry ice.

Analytical Procedures: Metal Analyses

Concentrations of Fe, Mn, Ni, Pb, Cd, Zn, Cr, and Cu in water (both dissolved and total), sediment, detritus, caddisflies, crayfish, and snails were determined with a Perkin Elmer model 403 atomic absorption spectrophotometer (AA). A blank was carried through all digestion and extraction procedures.

Preliminary analyses demonstrated that water samples for total and dissolved metals had to be concentrated ten times before all the metal concentrations were within the AA detection limit. Preliminary samples were concentrated 2, 4, 8, and 10 times by evaporation and each concentrated sample was analyzed for metals. Metal concentrations for each concentrate did not differ by amounts greater than the instrument error. Therefore, evaporation was found to be an acceptable procedure that did not contribute any significant error to the analyses.

Water samples, used for both total and dissolved metals analyses, were prepared according to EPA's suggested procedure (58) with some minor modifications. For the determination of total metals, a 250-ml aliquot was evaporated to dryness and then refluxed with 3 ml of concentrated HNO_3. The remaining residue was dissolved with 2 ml of 1:1 hydrochloric acid (HCl) and filtered. The volume was then brought up to 25 ml with glass-distilled water.

For the determination of dissolved metals, a 250-ml aliquot was evaporated to dryness. Two ml 1:1 HCl were added to dissolve the residue. The dissolved residue was then filtered and the volume brought up to 25 ml with glass distilled water.

Thawed sediment samples were dried at 100°C and then sieved through a 60-mesh (0.250 mm) polyethylene sieve. Metals from 6 g of sediment (dried to constant weight) were extracted with 0.5 N HCl to remove only those non-residual metals of an anthropogenic origin (59). The extraction was accomplished by shaking the sediment-acid mixture (80 ml 0.5 N HCl) for 12 hr at room temperature. After 12 hours, the mixture was filtered and the volume was brought up to 100 ml with glass-distilled water.

Detritus samples were dried at 100°C, pulverized with a mortar and pestle, and sieved through a 60-mesh, polyethylene sieve to obtain a consistent size fraction for analysis. Samples to be digested were dried to constant weight. Caddisflies were washed with glass-distilled water to remove any loose material, dried to constant weight at 100°C, and digested. Crayfish were classified according to the size of their carapace and dissected to obtain the tail muscle and remove the digestive tract. The tail muscle was dried to constant weight at 100°C, weighed, and digested. Snails were sorted to size (only those snails between 20 and 22 mm were used), removed from their shells, dried to constant weight at 100°C, and digested.

All biological materials were digested using a modification of Adrian's (60) wet-digestion method. The dried sample was placed in a 2 oz. acid-washed, polyethylene bottle with 1 ml of concentrated perchloric acid ($HClO_4$) and 2 ml concentrated HNO_3. The bottles were sealed tightly, and the samples were allowed to digest at room temperature for 15 hr and then for 2 hr in a water bath at 60°C. The caps were then removed, 2 ml of glass-distilled water were added, and the bottles were heated another 2 hr to expel any excess acid. Inert material present on the detritus and in the digestive tracts of the caddisflies and snails was removed by filtering the samples by procedures previously described. Crayfish samples did not require filtering, however.

Characterization of Sediments

Sediments were analyzed for organic matter; clay, silt, and sand fractions; and cation exchange capacity (CEC). Percent organic carbon was determined by a titration procedure (61) that measured the amount of oxidizable carbon in the sediment. Oxidation was accomplished with 1 N dichromate and concentrated sulfuric acid (H_2SO_4). Heat that is evolved from the addition of H_2SO_4 drives the reaction to completion. Percent organic carbon was then measured by titrating the excess dichromate with 0.5 N ferrous ammonium sulfate (FAS).

Percent sand, silt, and clay were determined by the hydrometer method according to the procedure (422D) specified by the American Society of Testing and Materials (62) using a 151 H soil test hydrometer. Approximately 30 g of dried sediment (< 60 mesh) were used for the analysis. The specific gravity of each soil suspension was measured at intervals of 0.5, 1, 2, 4, 8, 15, 30, 60, 120, 240, 400, and 720 minutes. Usually after 720 minutes, only clay particles (< 2µ) remain in suspension.

CEC was determined by measuring the exchangeable cations Ca, Mg, K, and H using a neutral ammonium acetate extraction (63). Ca, Mg, and K were determined by standard AA procedures. H was determined using a titration procedure. The results were expressed as the run of exchangeable cations in terms of milliequivalents per 100 grams sediment.

Other Water Analyses

Total and volatile suspended solids, total hardness, and alkalinity were determined in accordance with procedures prescribed by Standard Methods (64). Dissolved oxygen and temperature were measured with a YSI Model 54A Oxygen Meter. A Corning Model 610A portable pH meter was used for pH measurements. Concentrations of TOC were determined using an Envirotech-Dohrman Model 54 TOC Analyzer (sensitivity < 50 µg/l).

IV. RESULTS

The results of this study are presented in four sections. First, the various physical, chemical, and hydrological data for all stream stations and sampling dates are summarized. Second, variations of metal concentrations within all stream components are examined as functions of downstream distance. Third, relative metal accumulations within each stream component are compared. Fourth, relationships concerning the distribution of the various metals among the various stream components are examined. In some cases, figures and tables for only Pb and Cu are presented in this section for the sake of brevity. Similar figures and tables concerning the other metals can be found in the Appendix. However, these data are summarized in this section.

Appendix Tables A-1 through A-5 contain physical, chemical, and hydrological stream data monitored during the study period. Appendix Tables B-1 through B-6 contain metal concentration data for all stream components. Appendix Table C-1 contains data characterizing sediment by percent sand, silt, clay, and organic carbon. Appendix Figures D-1 through D-28 show variations of Fe, Mn, Ni, Cd, Zn, and Cr concentrations (and 95 percent confidence intervals) found in water, sediment, detritus, caddisflies, and crayfish as functions of downstream distance. Appendix Tables E-1 through E-6 present mean concentrations of Fe, Mn, Ni, Cd, Zn, and Cr in the stream components and the results of Duncan's Multiple Range Test for comparing the means among the six stream stations. Appendix Tables F-1 through F-6 contain correlation coefficients among stream components for the metals Fe, Mn, Ni, Cd, Zn, and Cr. Appendix Table G-1 contains metal concentrations and carapace lengths of crayfish.

Summary of Physical, Chemical, and Hydrological Data for Bull Run

A summary of the various physical, chemical, and hydrological data for the five sampling dates are tabulated by stream station in Table 5. Water at all stream stations exhibited average pH values ranging from 6.3 to 6.8. Note that the dissolved oxygen concentrations were lowest at Station 6 (3.8 mg/l) and highest at Station 2 (9.4 mg/l). Total alkalinity and hardness were highest at Station 5 (194 and 212 mg/l), and lowest at Station 2 for total alkalinity (47 mg/l), and Stations 1 and 3 for hardness (58 mg/l). Total organic carbon was found to be highest at Station 6 (81 mg/l), which correlates well with the low D.O. concentrations there, and lowest at Station 2 (8.2 mg/l). There was no distinct difference in total and volatile suspended solids concentrations at the six stream stations. Average stream flow at Station 6 was 15.3 cfs--some 80 times that at Station 1.

Variation of Metal Concentration with Downstream Distance

Lead and Copper. Figures 2 through 6 show means and 95 percent confidence intervals for Pb concentrations in unfiltered water (total Pb), sediment, detritus, caddisflies and crayfish as functions of downstream distance. Mean Pb concentrations in water, sediment, detritus, and caddisflies were shown to increase with downstream distance. Moreover, mean Pb concentrations in these components at distances

Table 5

Summary of Physical, Chemical, and Hydrological Stream Data for the Five Sampling Dates from July 30 to October 2, 1977. All Values in mg/l Except Where Noted

	Stream Station[a]											
	1		2		3		4		5		6	
Parameter	Avg.	Range	Avg.	Range	Avg.	Range	Avg.	Range	Avg.	Range	Avg.	Range
pH	6.6	5.5 - 7.2	6.8	6.3 - 7.2	6.5	6.0 - 7.2	6.4	5.8 - 6.8	6.6	6.0 - 7.2	6.3	6.1 - 6.5
Temperature, °C	24	20 - 29	24	19 - 28	25	21 - 29	24	19 - 29	25	21 - 28	23	19 - 26
Dissolved Oxygen	6.7	5.0 - 9.1	7.7	7.0 - 9.4	6.8	5.0 - 8.2	6.1	4.7 - 7.5	6.1	4.8 - 8.3	4.9	3.8 - 6.3
Total Alkalinity	68	57 - 77	67	47 - 78	65	49 - 74	74	67 - 92	129	78 - 194	85	64 - 117
Total Hardness	73	62 - 80	79	58 - 98	77	58 - 86	114	95 - 150	179	130 - 212	136	109 - 184
Total Organic Carbon	13	10 - 16	12	8 - 16	13	10 - 14	17	10 - 25	17	12 - 20	28	9 - 81
Total Sus. Solids	8	4 - 12	7	2 - 10	6	3 - 10	9	4 - 12	7	3 - 12	7	5 - 11
Vol. Sus. Solids	2	1 - 4	2	1 - 3	2	1 - 2	2	1 - 3	2	1 - 2	2	1 - 3
Gage Height, ft.	1.55	1.44 - 1.60	--	--	--	--	1.30	1.24 - 1.38	--	--	0.95	0.85 - 1.12
Flow, cfs	0.21	0.03 - 0.62	--	--	--	--	6.6	5.0 - 9.8	--	--	15.3	10.0 - 26

[a] See Figure 1, in text.

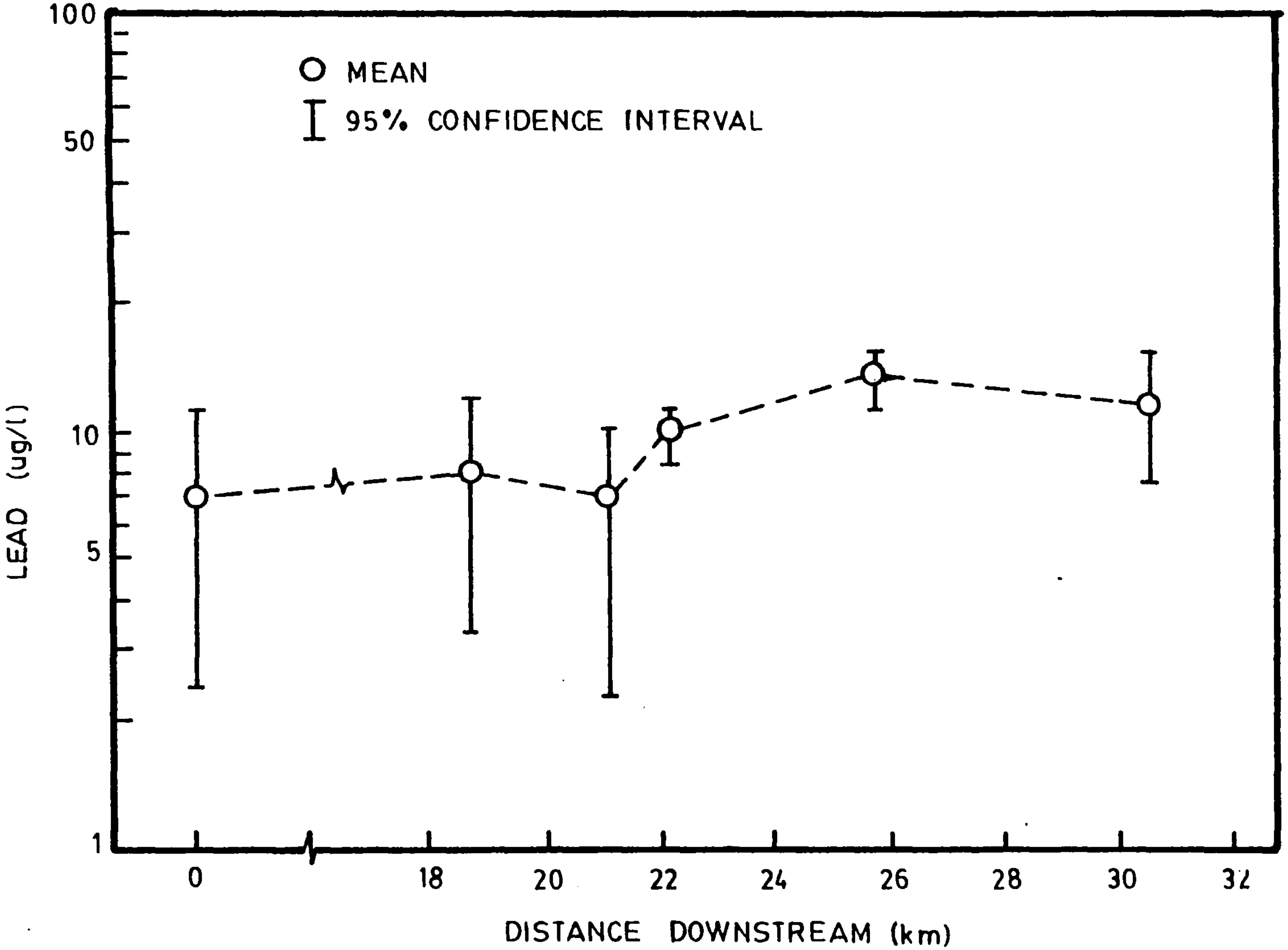


Figure 2. Total lead concentrations in water at all six Bull Run stream stations.

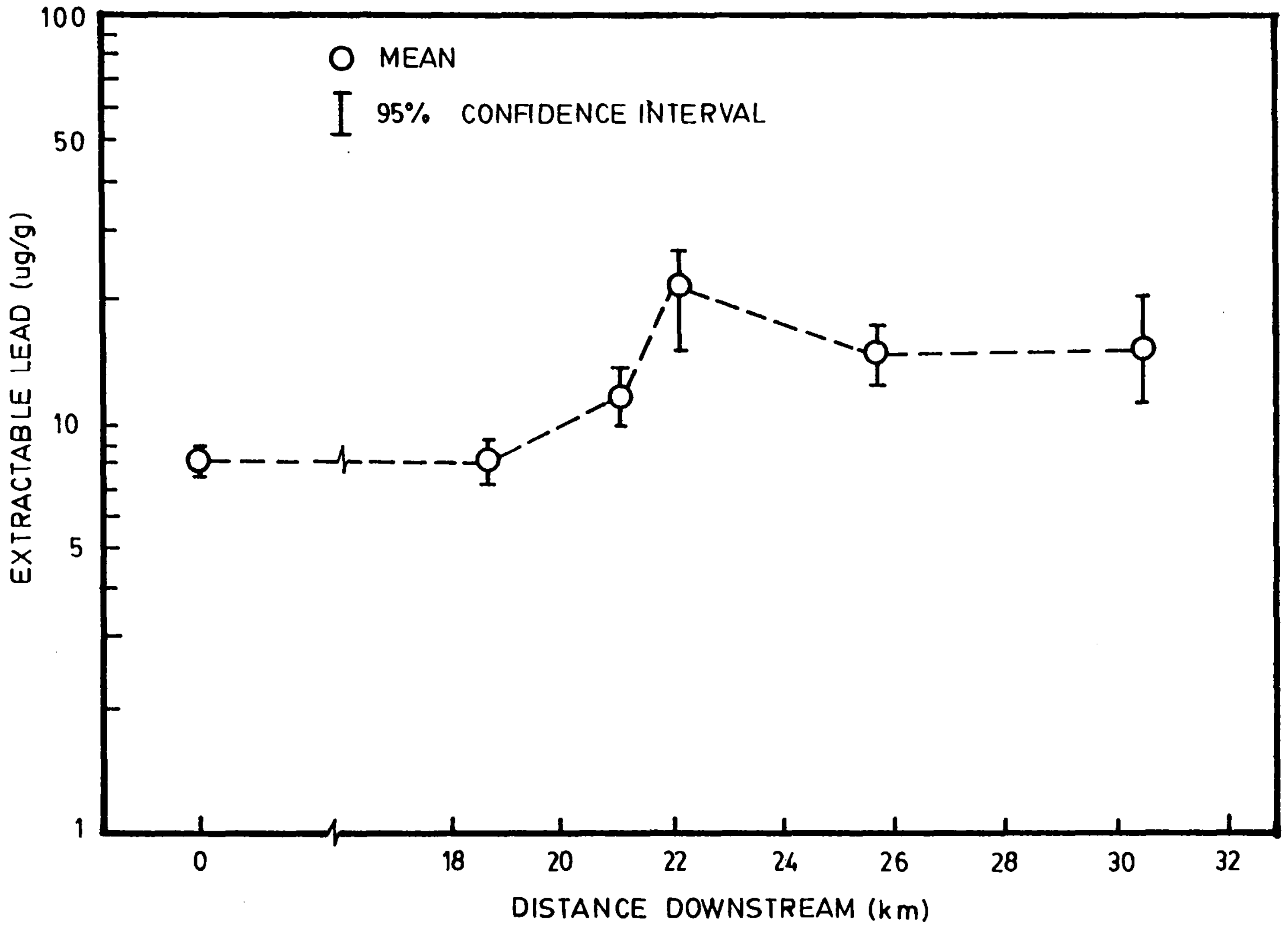


Figure 3. Extractable lead in sediments from all six Bull Run stream stations.

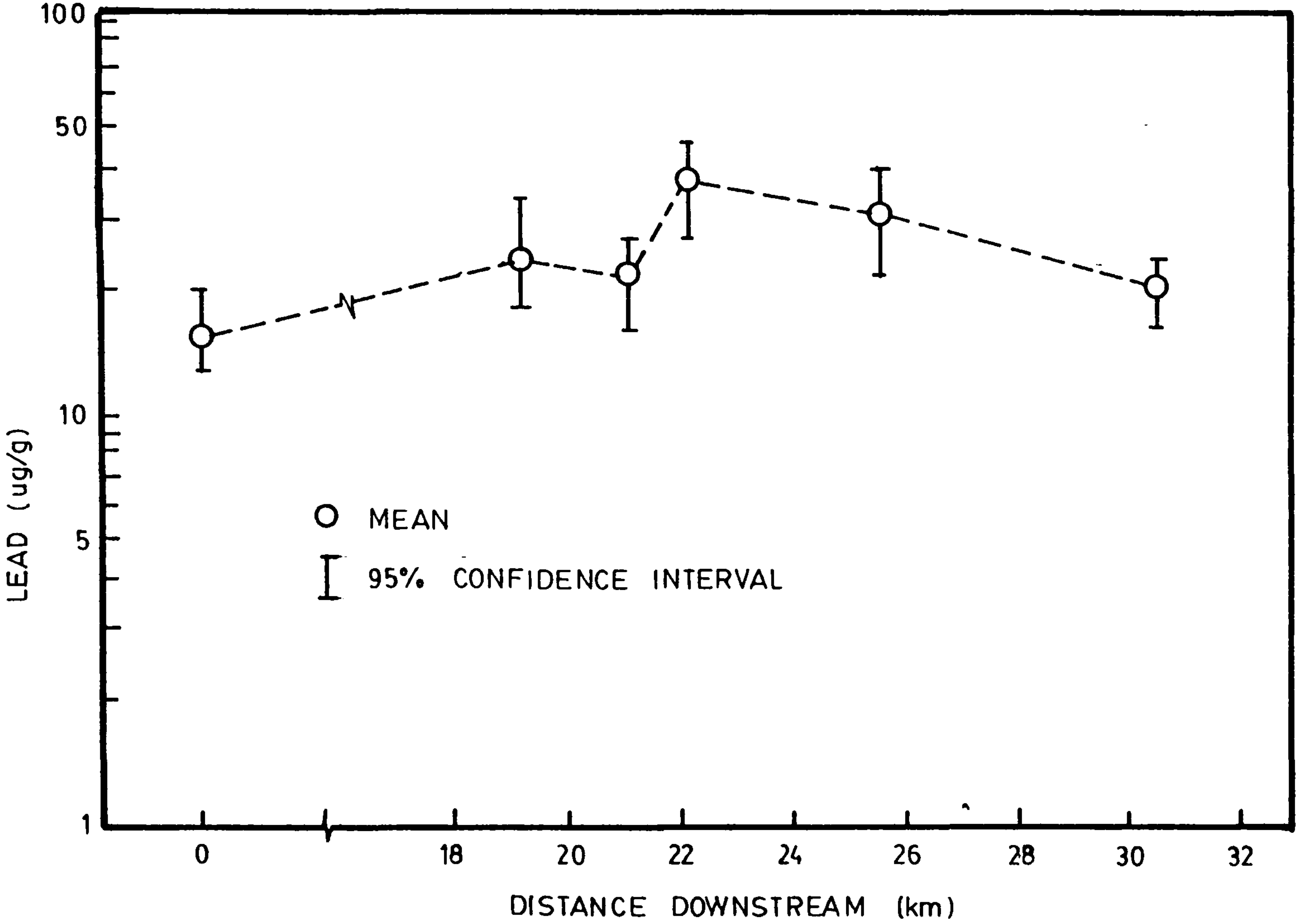


Figure 4. Lead concentrations in detritus from all six Bull Run stream stations.

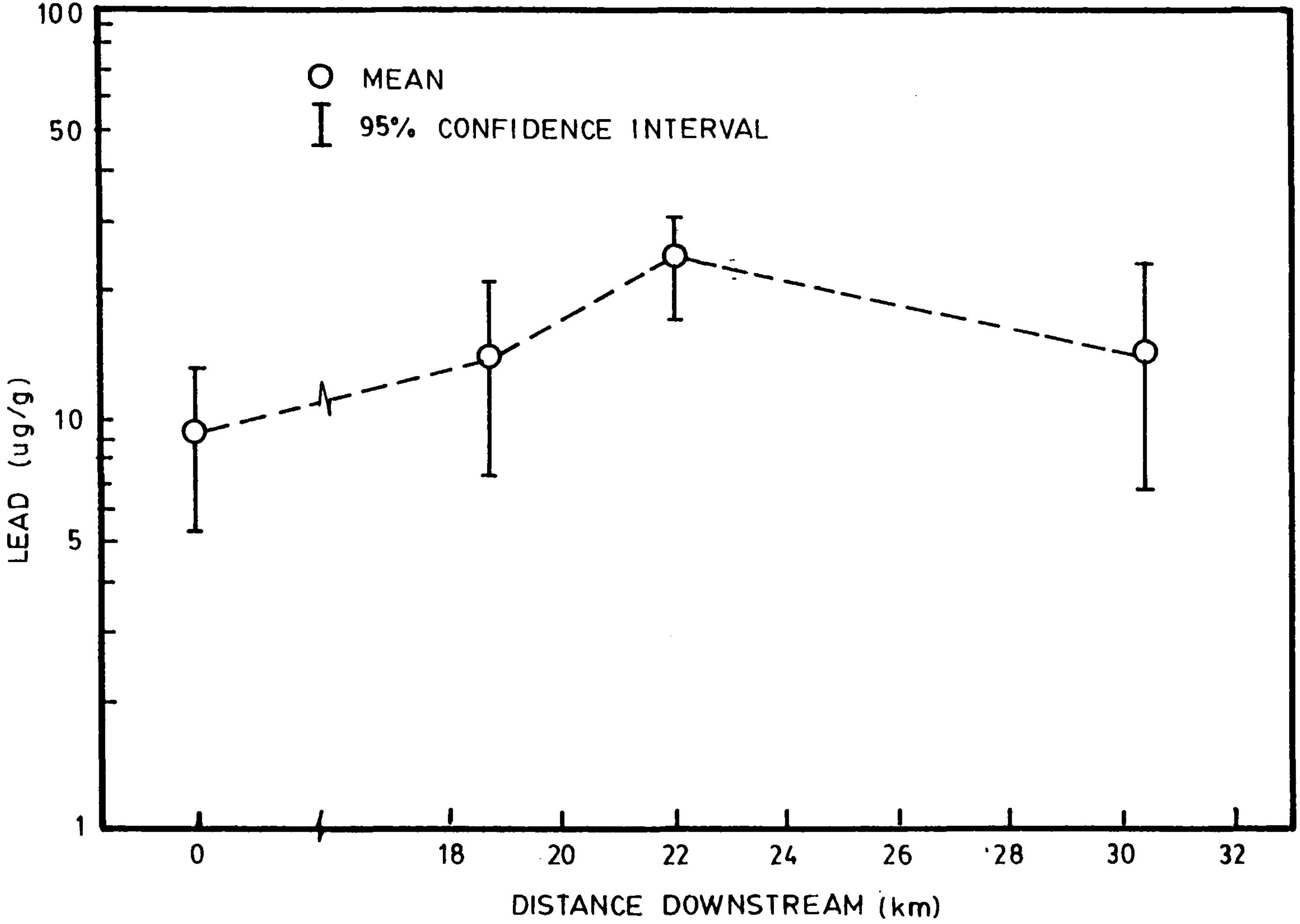


Figure 5. Lead concentrations in caddisflies from Bull Run Stations 1, 2, 4, and 6.

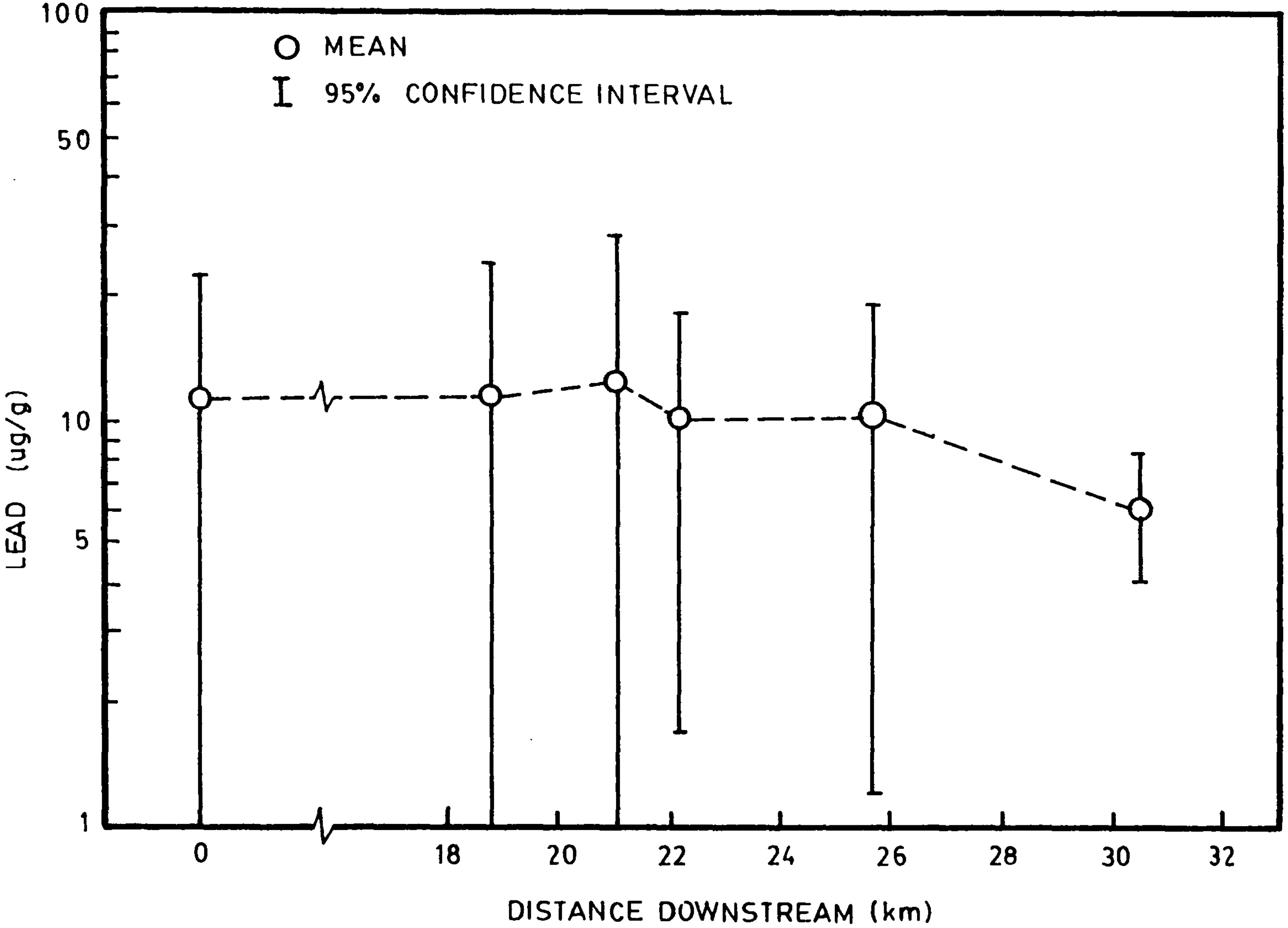


Figure 6. Lead concentrations in crayfish from all six Bull Run stream stations.

greater than 22 km (Station 4) were shown to be greater than at the upstream control, Station 1. Mean Pb concentrations in crayfish, however, displayed a decreasing trend with downstream distance.

Mean Pb concentrations in all stream components and the results of Duncan's Multiple Range Test for comparing differences of these means among the six stream stations appear in Table 6. Means connected by brackets are not statistically different at the 0.95 level. Although the calculated means may be different in these cases, significant differences could not be determined because of the large variability that existed for a particular set of observations. The degree of variability is reflected by the size of the 95 percent confidence intervals plotted on Figures 2 through 6. It is very important to consider, however, that while mean metal concentrations in a stream component may not be statistically different among stream stations, one should not ignore downstream trends that are demonstrated by these figures.

From Table 6, one should note that at Station 4 (immediately below the stormwater input from Flat Branch), Pb concentrations in sediment, detritus, and caddisflies were greater than at any other station. Moreover, Pb concentrations for these components were statistically greater at this downstream station than at the upstream control, Station 1. (No snails were found at Stations 1 and 4.) Whereas total Pb concentrations in water were not greatest at Station 4, Pb concentrations for these components were greatest at the downstream Stations 5 and 6, and at these stations, Pb concentrations were significantly greater than at the upstream control, Station 1. Thus, while the total

Table 6

Mean Lead Concentrations for All Stream Components and the Results of Duncan's Multiple Range Analysis for Comparing Differences of These Means Among the Stream Stations

Stream Component	Stream Station and Corresponding Mean Lead Concentration*					
Dissolved Lead, μg/l	5	6	4	2	1	3
	14.0	9.5	8.6	5.4	4.6	4.4
Total Lead, μg/l	5	6	4	2	1	3
	14.0	12.0	10.2	8.0	7.0	6.6
Sediment, μg/g	4	6	5	3	1	2
	21.6	16.1	15.6	12.0	8.2	8.2
Detritus, μg/g	4	5	2	3	6	1
	36.1	31.0	23.6	21.9	21.1	16.2
Caddisflies, μg/g	4	6	2	1		
	24.2	14.6	14.0	9.2		
Snails, μg/g	2	6				
	7.4	7.0				
Crayfish, μg/g	3	2	1	5	4	6
	12.9	11.4	11.4	10.3	10.1	6.1

*Means connected by the same bracket are not significantly differend from each other at the 0.95 level.

Pb concentration in water at Station 4 (22 km point) was not statistically different than at Station 1 (0 km point), it is evident from Figure 2 that the mean total Pb concentration in water did increase in the downstream direction.

Figure 6 shows the large variability of Pb concentrations in crayfish, and the apparent decrease of the mean concentrations with downstream distance. This large variability influences the results shown in Table 6 where the mean Pb concentrations in crayfish for all stations (connected by one bracket) were not found to be statistically different.

Figure 7 through 12 show the means and 95 percent confidence intervals for Cu concentrations in unfiltered water (total Cu), sediment, detritus, caddisflies, and crayfish, as functions of downstream distance. Mean Cu concentrations in sediment, detritus, caddisflies, and crayfish were shown to increase with downstream distance. Moreover, mean Cu concentrations for these components at distances greater than 22 km (i.e., beyond Station 4) were shown to be greater than at the upstream control, Station 1.

Mean Cu concentrations in all stream components and the results of Duncan's Multiple Range Test for comparing differences of these means among the six stream stations appear in Table 7. Mean total and dissolved Cu concentration in water, and Cu concentrations in sediment, detritus, and caddisflies were greatest immediately below Flat Branch at Station 4 than at the upstream control, Station 1. In fact, Cu concentrations in sediment, detritus, and caddisflies were

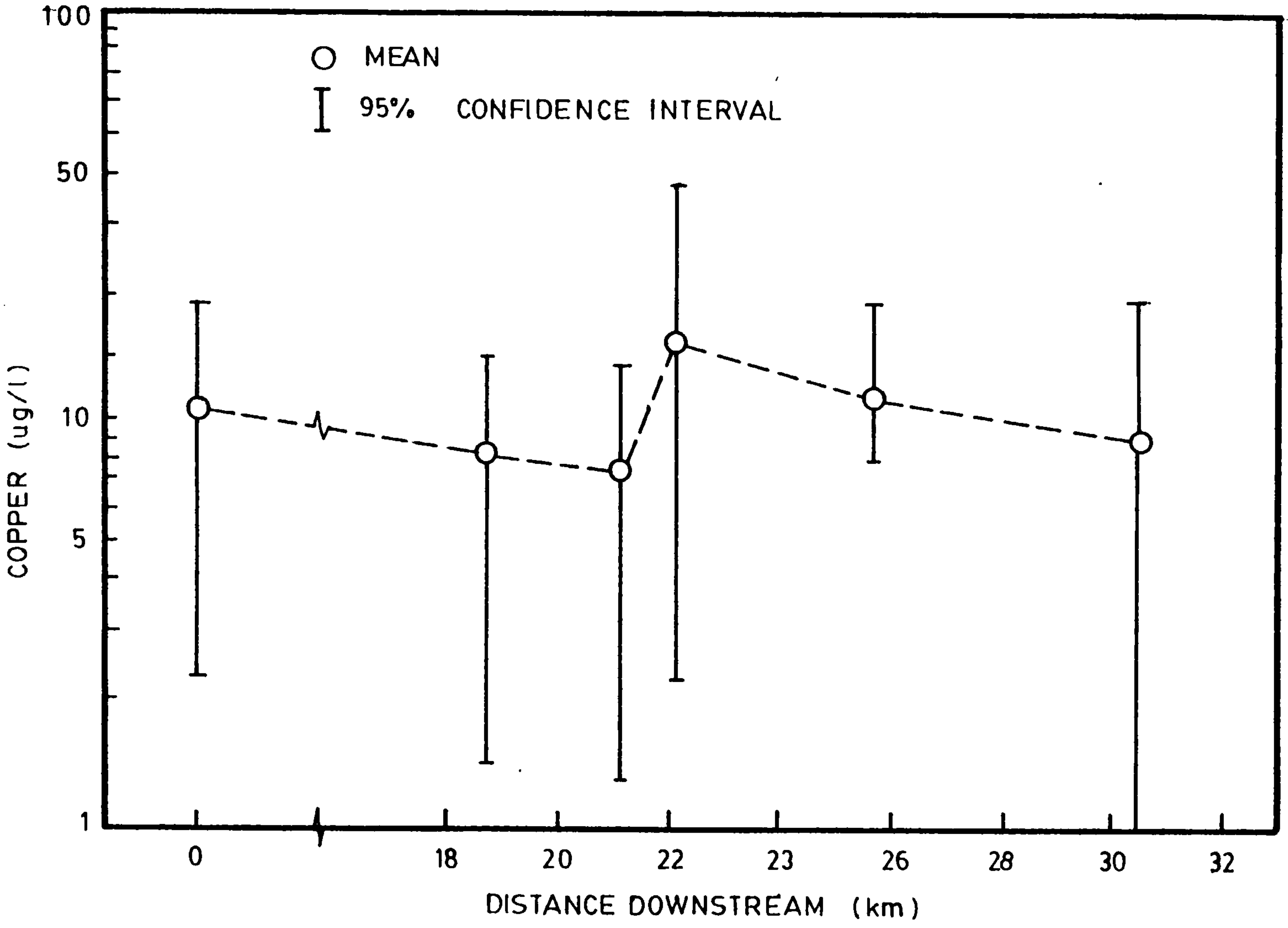


Figure 7. Total copper concentrations in water for all six Bull Run stream stations.

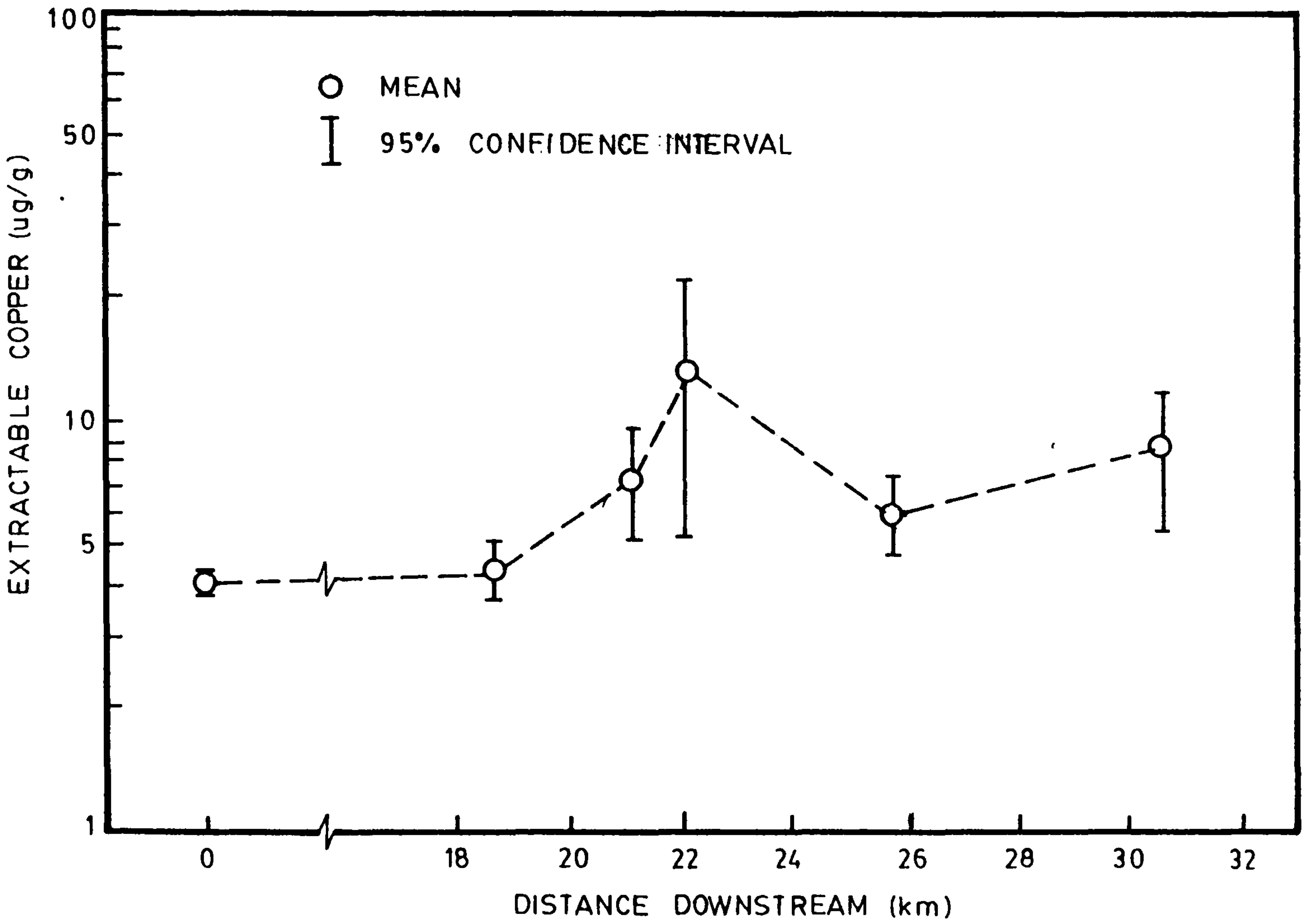


Figure 8. Extractable copper in sediments from all six Bull Run stream stations.

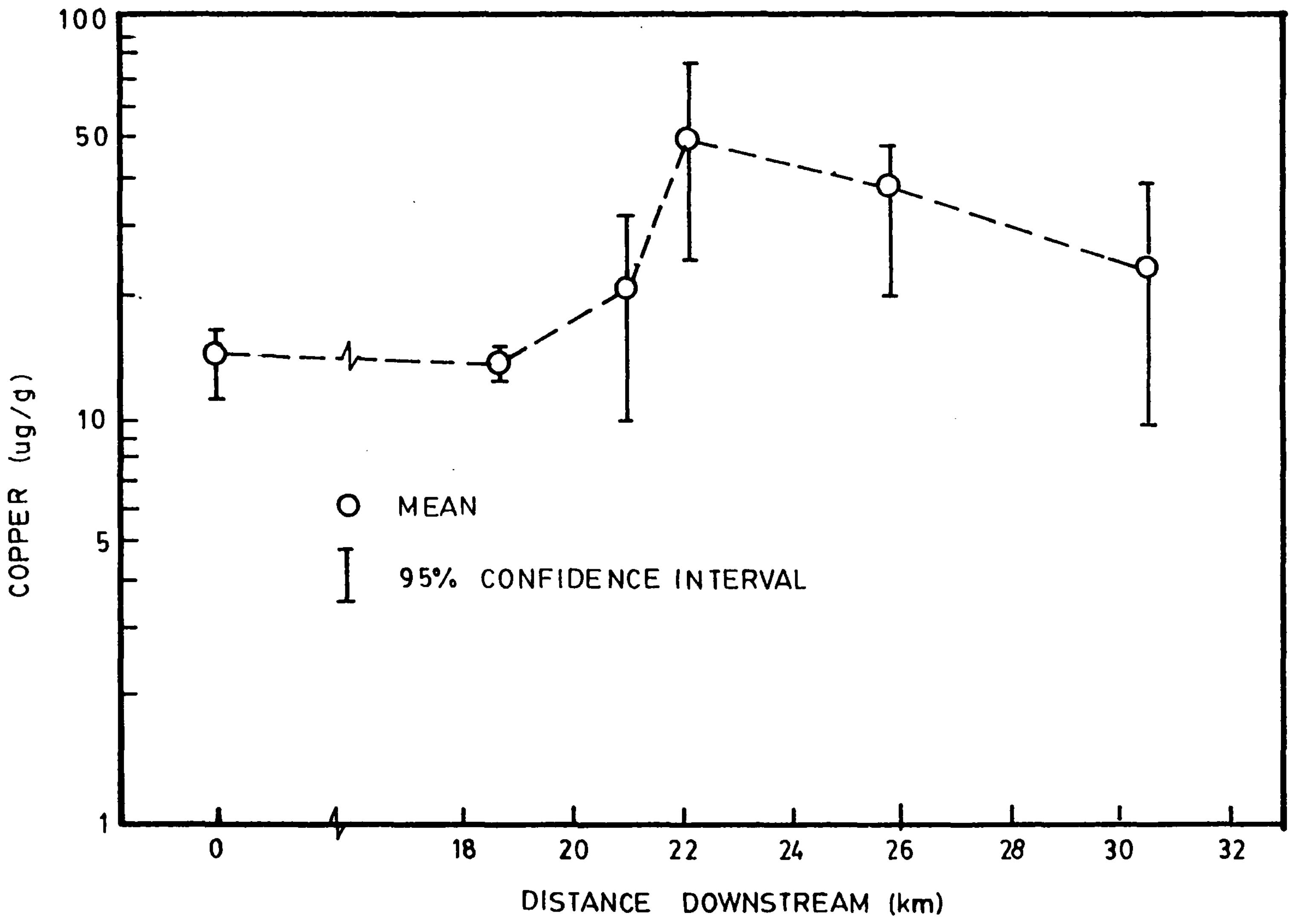


Figure 9. Copper concentrations in detritus from all six Bull Run stream stations.

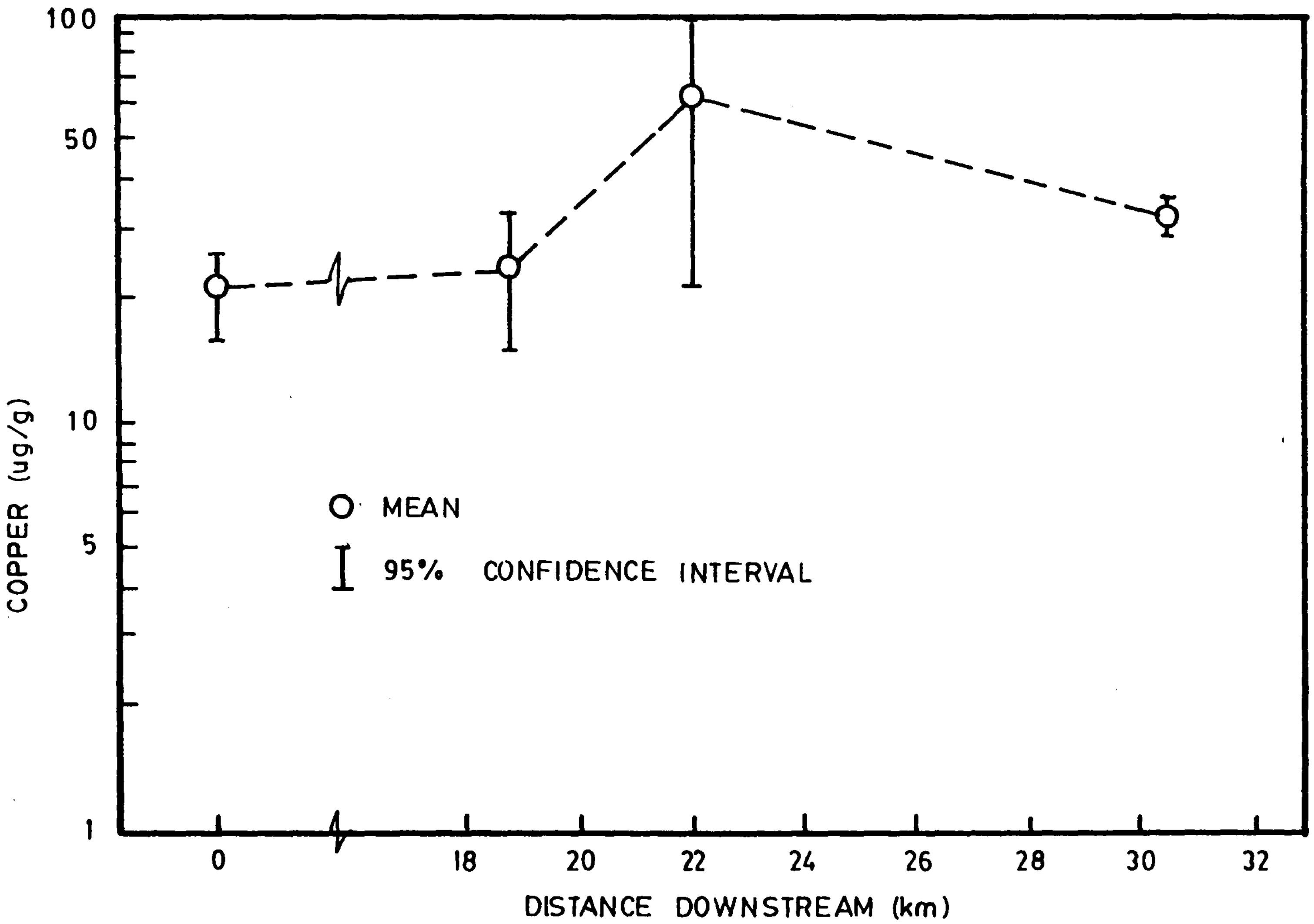


Figure 10. Copper concentrations in caddisflies from Bull Run Stations 1, 2, 4, and 6.

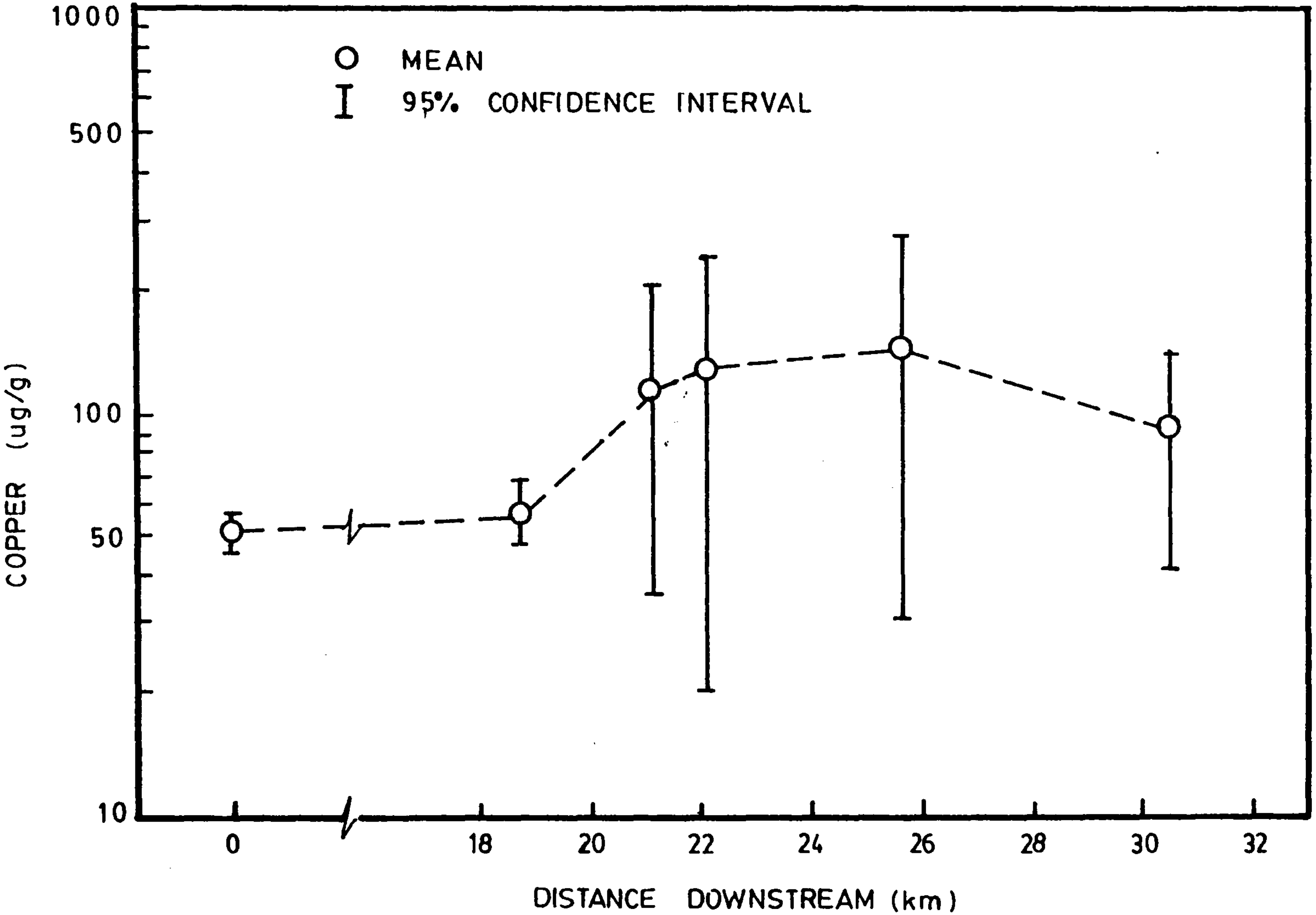


Figure 11. Copper concentrations in crayfish from all six Bull Run stream stations.

Table 7

Mean Copper Concentrations for All Stream Components and the Results of Duncan's Multiple Range Analysis for Comparing Differences of These Means Among the Stream Stations

Stream Component	Stream Station and Corresponding Mean Copper Concentrations*					
Dissolved Copper, µg/l	4	5	1	6	2	3
	10.0	8.8	3.8	3.3	2.2	1.8
Total Copper, µg/l	4	5	1	6	2	3
	16.6	11.8	10.8	9.3	8.4	7.8
Sediment, µg/g	4	6	3	5	2	1
	13.7	8.9	7.3	6.1	4.4	4.1
Detritus, µg/g	4	5	6	3	1	2
	51.7	39.3	24.2	21.1	14.5	14.4
Caddisflies, µg/g	4	6	2	1		
	60.9	31.0	23.8	21.1		
Snails, µg/g	6	2				
	14.6	82.4				
Crayfish, µg/g	5	4	3	6	2	1
	151	130	118	92.7	55.5	51.5

*Means connected by the same bracket are not statistically different from each other at the 0.95 level.

significantly greater at Station 4 than at Station 1. Although mean total Cu concentrations in water were greatest at Station 4, the variability (Figure 7) was large enough so that differences among the means were not statistically significant (Table 7).

Cu concentrations in snails were also greater downstream at Station 6 than upstream at Station 2, and this difference was seen to be significant (Table 7). Figure 11 shows that crayfish downstream of the 21.1 km point (Station 3) concentrated Cu more than those at the two upstream stations (1 and 2). Although this phenomenon appears to have persisted in the downstream direction, the variability was such that only Cu concentrations in crayfish at Station 5 were significantly greater than at Station 1 (Table 7). Similarly, Cu in caddisflies is seen (Figure 11) to be in greater concentration at the downstream Stations 4 and 6 than at the upstream Stations 1 and 2. (No caddisflies were collected at Stations 3 and 5.) Statistically, however, Cu concentrations in caddisflies at Station 6 were no different from those at Stations 1 and 2. Therefore, while Cu concentrations in some components at the downstream stations were not statistically different from those at the upstream stations, Figures 7 through 11 show there were greater Cu concentrations at Station 4 than at Station 1. There appears to be some recovery at Stations 5 and 6, however. With the exception of total Cu in water (Figure 7), mean Cu concentrations in the other stream component at the downstream Stations 5 and 6 are shown to be greater than at the upstream control, Station 1 (see Figures 8-11).

Other Metals. Means and 95 percent confidence intervals for the other metals (Fe, Mn, Ni, Cd, Zn, Cr) in water, sediment, detritus, caddisflies, and crayfish are plotted as functions of downstream distance in Appendix Figures D1 through D28. For a majority of stream components, concentrations of these metals did not show a distinct increasing trend with downstream distances as was evident for Pb and Cu.

Table 8 summarizes the trends of metal concentrations (Fe, Mn, Ni, Cd, Zn, Cr) in water, sediment, detritus, caddisflies, and crayfish with increasing distance downstream. The terms "definite," "slight," and "no change" are subjective and the reader is advised to consult Appendix Figures D1 through D28 for a more complete analysis. However, using Table 8 as a guide, one should note that the concentration trends "decrease" and "no change" best characterize the concentrations of Fe, Mn, and Ni. The concentrations of Cd, Zn, and Cr demonstrated some increasing trends for sediment and detritus. Cd and Cr concentrations were zero in crayfish.

These trends are also reflected by the statistical analysis of the differences of means for stream components among the six stations. Table 9 is a summary of Duncan's Multiple Range Test for these metals (Fe, Mn, Ni, Cd, Zn, Cr). Mean concentrations and the results of Duncan's Multiple Range Test for each metal are presented in Appendix Tables E1 through E6. Table 9 is only a summary and the reader is again advised to consult the appendix tables for a more complete analysis.

As one can see, the differences among metal concentrations in sediment and detritus were more significant among the stream stations

Table 8

Summary of Trends Exhibited by the Metals Fe, Mn, Ni, Cd, Zn, and Cr with Increasing Distance Downstream

		Trend in Concentration Changes with Downstream Distance				
		Increase		Decrease		
Metal	Stream Components	Definite	Slight	Definite	Slight	No Change
Fe	Detritus		X			
	Sediment, Crayfish			X		
	Water				X	
	Caddisflies					X
Mn	Water, Crayfish	X				
	Sediment			X		
	Caddisflies				X	
	Detritus					X
Ni	Sediment, Crayfish			X		
	Water, Caddisflies				X	
	Detritus					X
Cd[a]	Sediment, Detritus	X				
	Caddisflies		X			
	Water					X
Zn	Sediment	X				
	Detritus		X			
	Water				X	
	Caddisflies, Crayfish					X
Cr[a]	Detritus	X				
	Sediment		X			
	Water, Caddisflies					X

[a] Cr and Cd concentrations in crayfish were zero.

Table 9

Summary of Duncan's Multiple Range Test for the Metals Fe, Mn, Ni, Cd, Zn, and Cr

	Ranked Order of Stations[a]						
Metal	Dissolved Metal in Water	Total Metal in Water	Sediment	Detritus	Caddisflies	Snails	Cray-fish
Fe	ND	ND	(2)>(1,4)>(3,6)>(5)	(4,5,1,2)>(3)	ND	ND	ND
Mn	(6,5,4)>(3,2,1)	(6)>(4,3)	(4.2)>(6,3,5)	(1,6,5,4,2)>(3)	(2)>(6)	(2)>(6)	ND
Ni	ND	ND	(2,1)>(6,4,3)>(5)	(4)>(3)	(1,6)>(4,2)	ND	ND
Cd	ND	ND	(4)>(2,3,5,1)	(6,4)>(5)	ND	ND	ND
Zn	(1)>(3,6,5)	ND	(4,6)>(1,3,2,5)	ND	ND	ND	ND
Cr	ND	ND	(2)>(6,3,4,1)>(5)	(4)>(3)	ND	ND	ND

[a] Numbers refer to mean metal concentrations at a particular station. Those station means enclosed by parentheses are not significantly different. ND signifies no significant difference could be found among mean metal concentrations among the six stream stations.

than in the other stream components. One should also note that metal concentrations in sediment were generally lowest at Station 5. Cd and Zn concentrations in sediment generally increased with downstream distance and were also found to be significantly greater downstream at Station 4 than upstream at Station 1.

Relative Metals Accumulation for Stream Components

Water. Table 10 shows means and ranges for total metal concentrations in water by stream station for all eight metals. Generally, total metal concentrations in water followed the order Fe > Mn > Ni > Zn > Cu > Pb > Cr > Cd. Fe concentrations were found to be as great as 900 μg/l while Cd concentrations were only found to be 1 μg/l.

Figures 12 through 19 show the relationships of total (unfiltered) and dissolved (filtered through a glass-fiber filter) for each metal and each stream station. Most of the Fe found in the water was removed by filtration so that dissolved Fe concentrations were 25 to 35 percent of the total at all stream stations. For Mn, however, 30 percent of the total was filterable at Station 1, but this increased to approximately 80 percent at Station 6. Dissolved Ni concentrations ranged from approximately 10 percent of the total at Station 1 to 30 percent at Station 5. Most of the Pb found in the water could be filtered so that dissolved Pb concentrations ranged from 68 percent of the total at Station 1 to 100 percent at Station 5. Dissolved Cd concentrations accounted for all of the Cd at the six stations. About half the Zn found in the water could be filtered so that dissolved Zn comprised 45 to 65 percent of the

Table 10

Mean Total Metals Concentration in Water for All Six Bull Run Stream Stations

Stream Station	Total Metal Concentration, μg/l (Mean and Range)							
	Fe	Mn	Ni	Pb	Cd	Zn	Cr	Cu
1	550	163	48	7	1	36	3	11
	263 - 900	90 - 193	9 - 106	3 - 12	1 - 1	17 - 55	1 - 3	5 - 22
2	445	143	41	8	1	32	3	8
	174 - 810	46 - 235	8 - 85	5 - 14	1 - 1	13 - 52	1 - 5	3 - 17
3	437	82	32	7	1	28	3	8
	270 - 773	48 - 119	2 - 79	2 - 11	1 - 1	16 - 48	1 - 4	4 - 17
4	436	140	29	10	1	32	3	17
	226 - 627	68 - 189	2 - 64	9 - 12	1 - 1	8 - 49	1 - 4	6 - 35
5	325	170	22	14	1	24	3	12
	202 - 550	137 - 230	9 - 41	12 - 16	1 - 1	1 - 40	2 - 3	9 - 16
6	479	234	32	12	1	29	3	9
	345 - 693	120 - 370	4 - 60	8 - 14	1 - 1	23 - 37	2 - 4	5 - 18

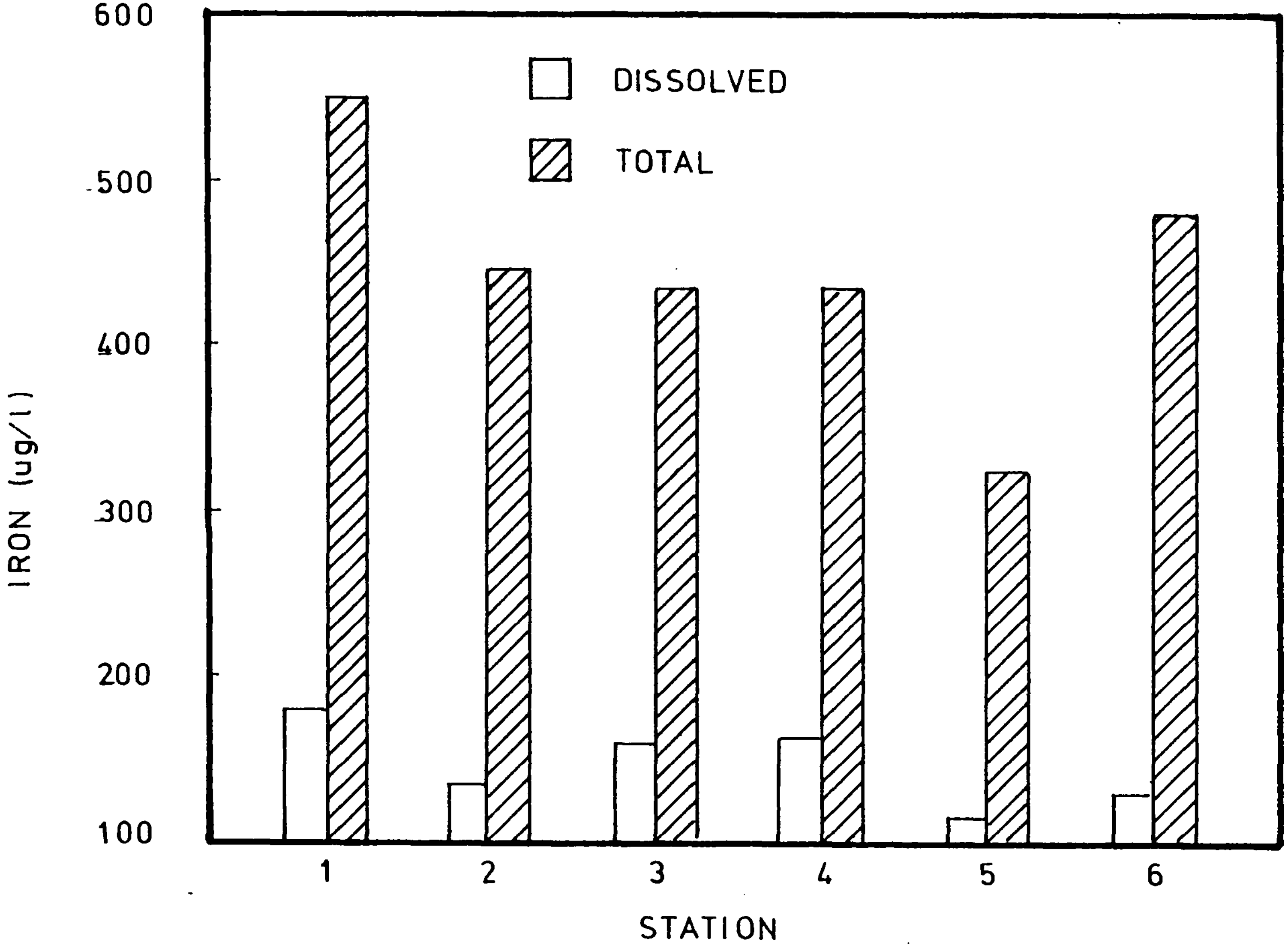


Figure 12. Total (unfiltered) and dissolved (filtered) iron concentrations in water for all six Bull Run stream stations.

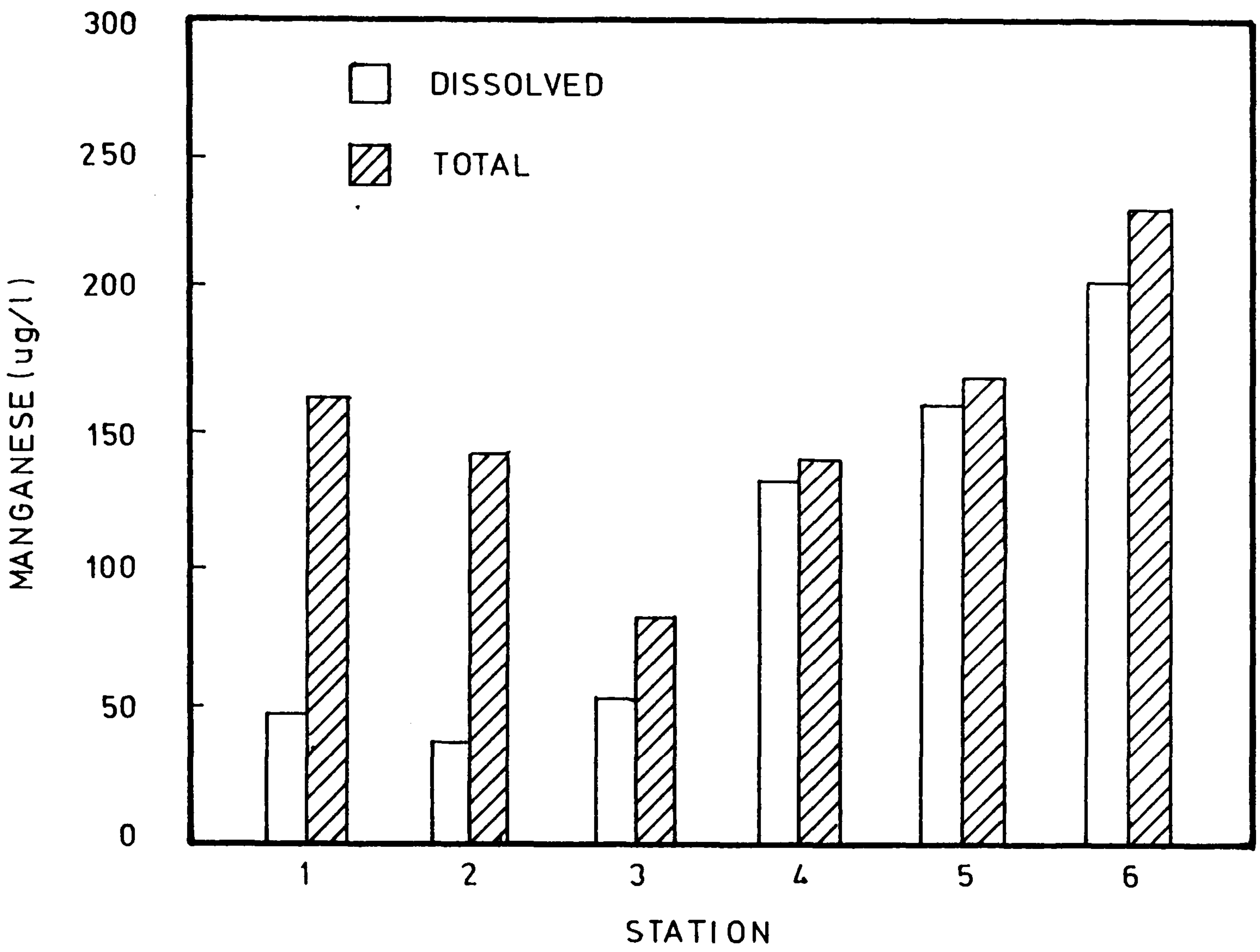


Figure 13. Total (unfiltered) and dissolved (filtered) manganese concentrations in water for all six Bull Run stream stations.

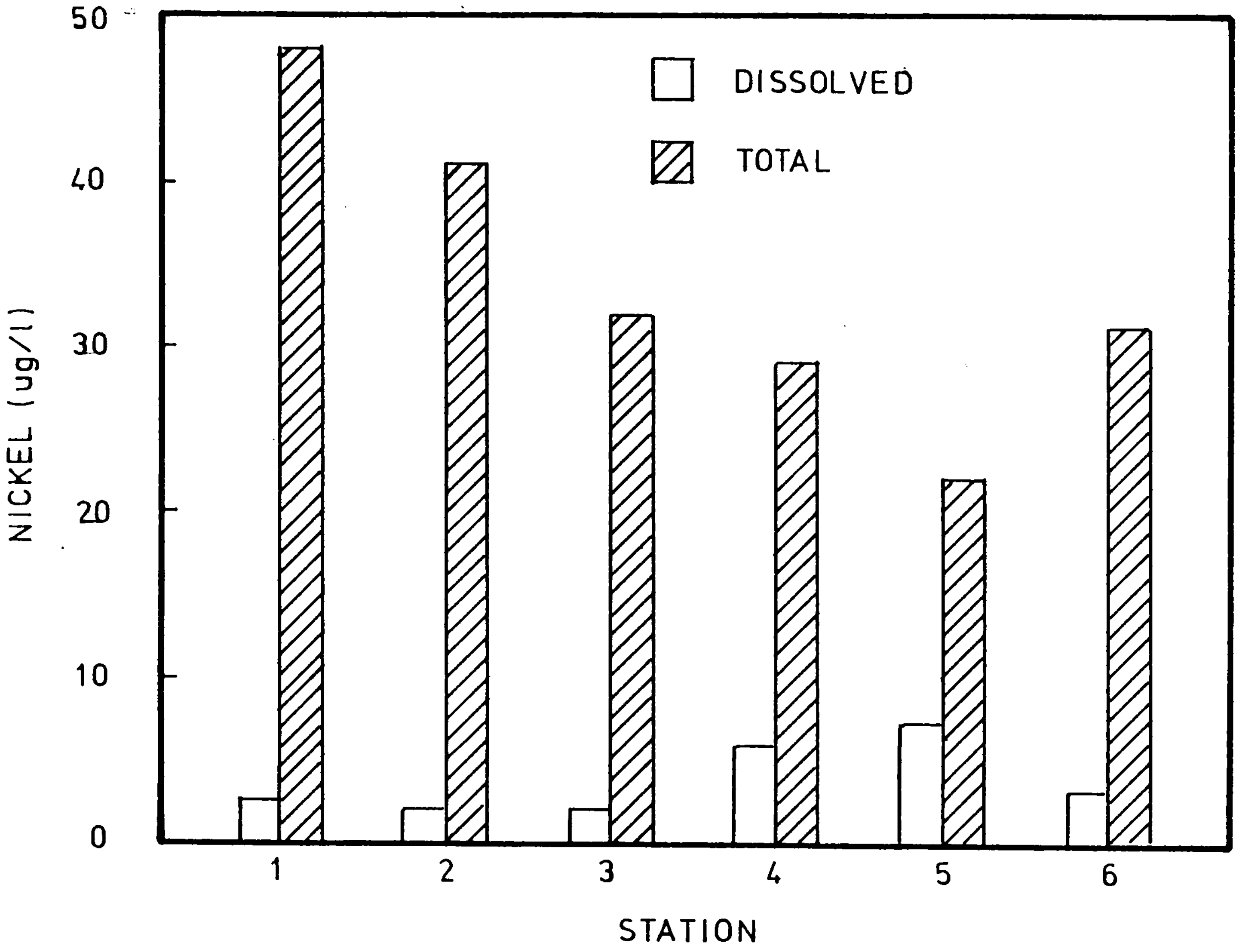


Figure 14. Total (unfiltered) and dissolved (filtered) nickel concentrations in water for all six Bull Run stream stations.

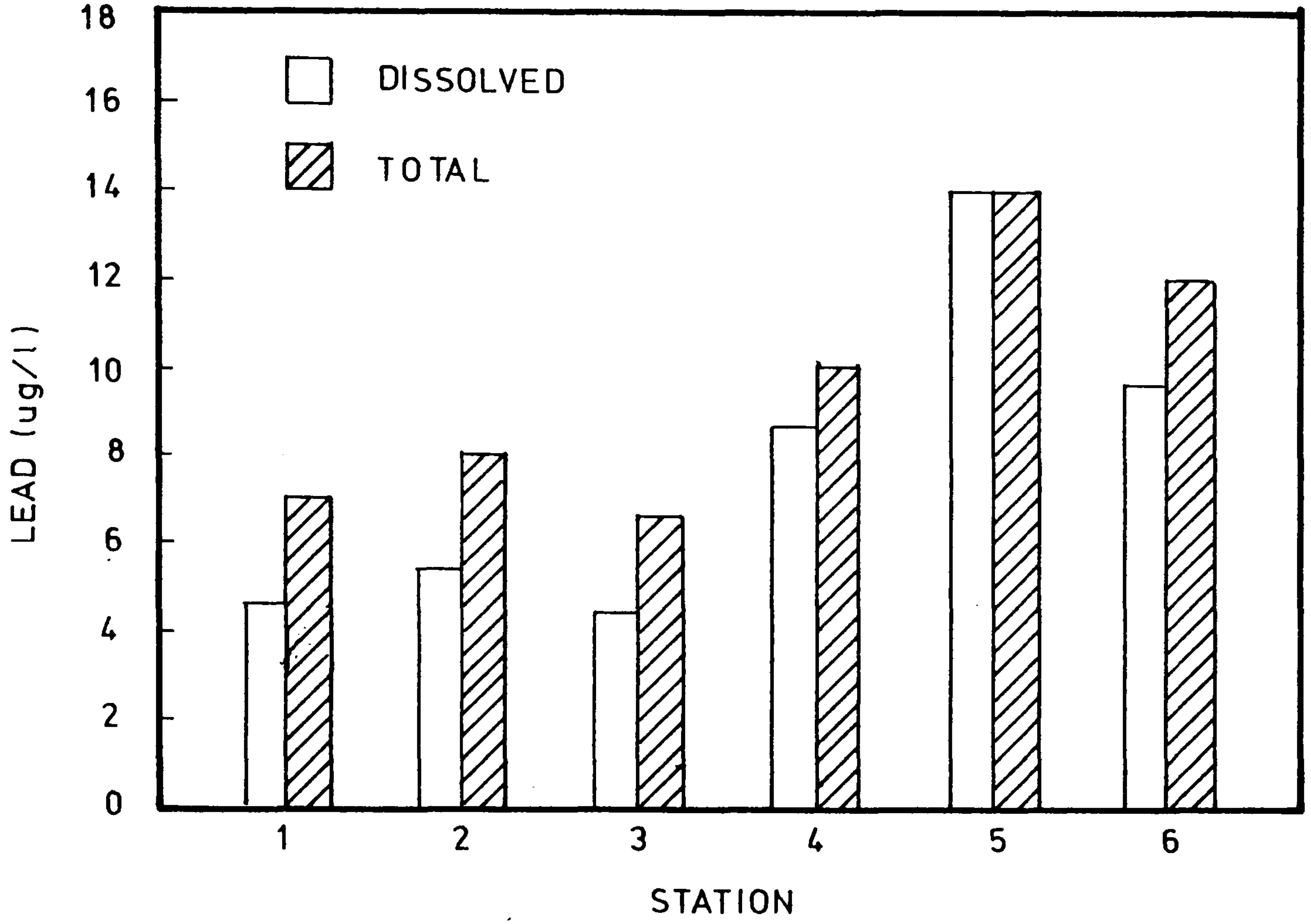


Figure 15. Total (unfiltered) and dissolved (filtered) lead concentrations in water for all six Bull Run stream stations.

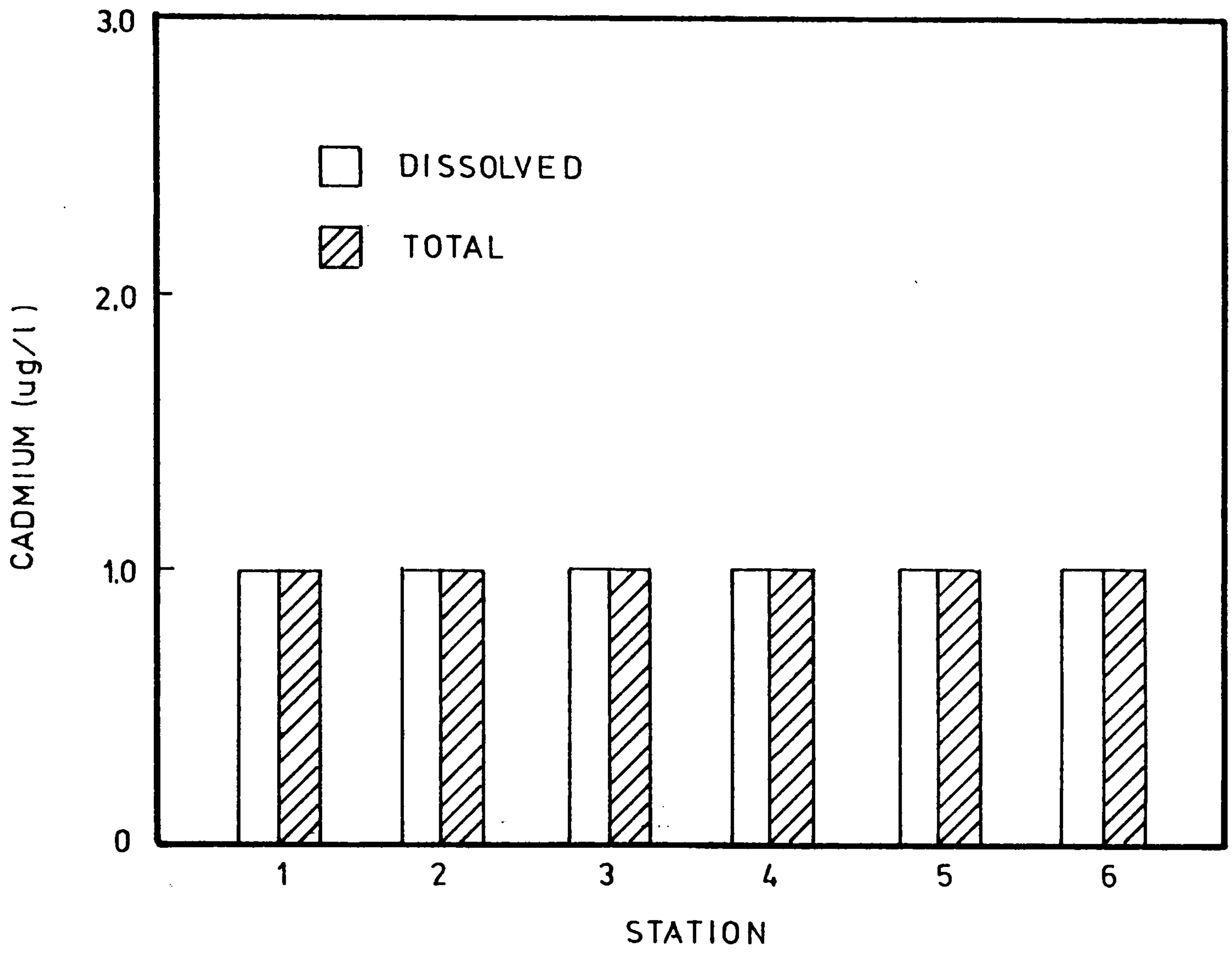


Figure 16. Total (unfiltered) and dissolved (filtered) cadmium concentrations in water for all six Bull Run stream stations.

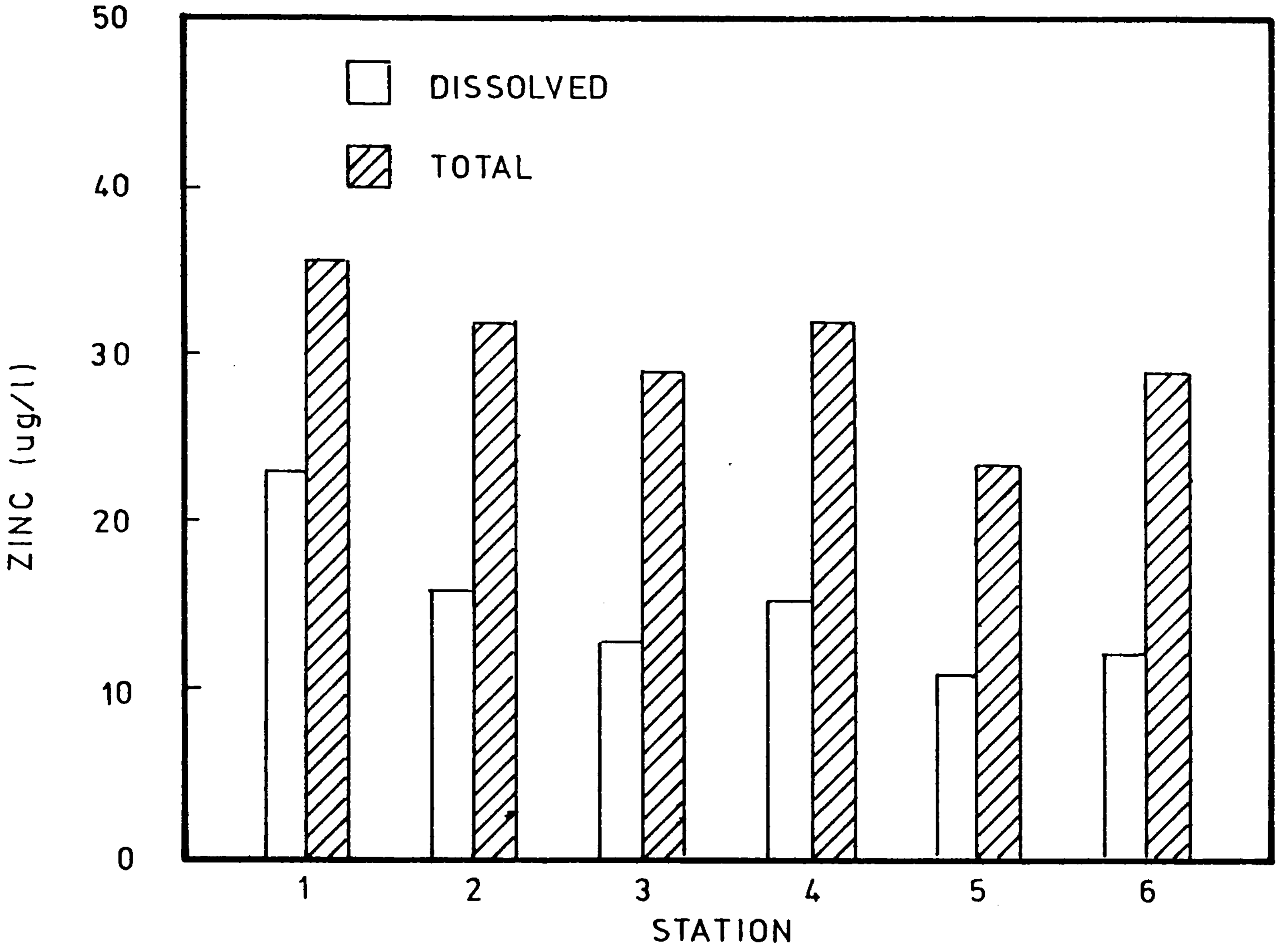


Figure 17. Total (unfiltered) and dissolved (filtered) zinc concentrations in water for all six Bull Run stream stations.

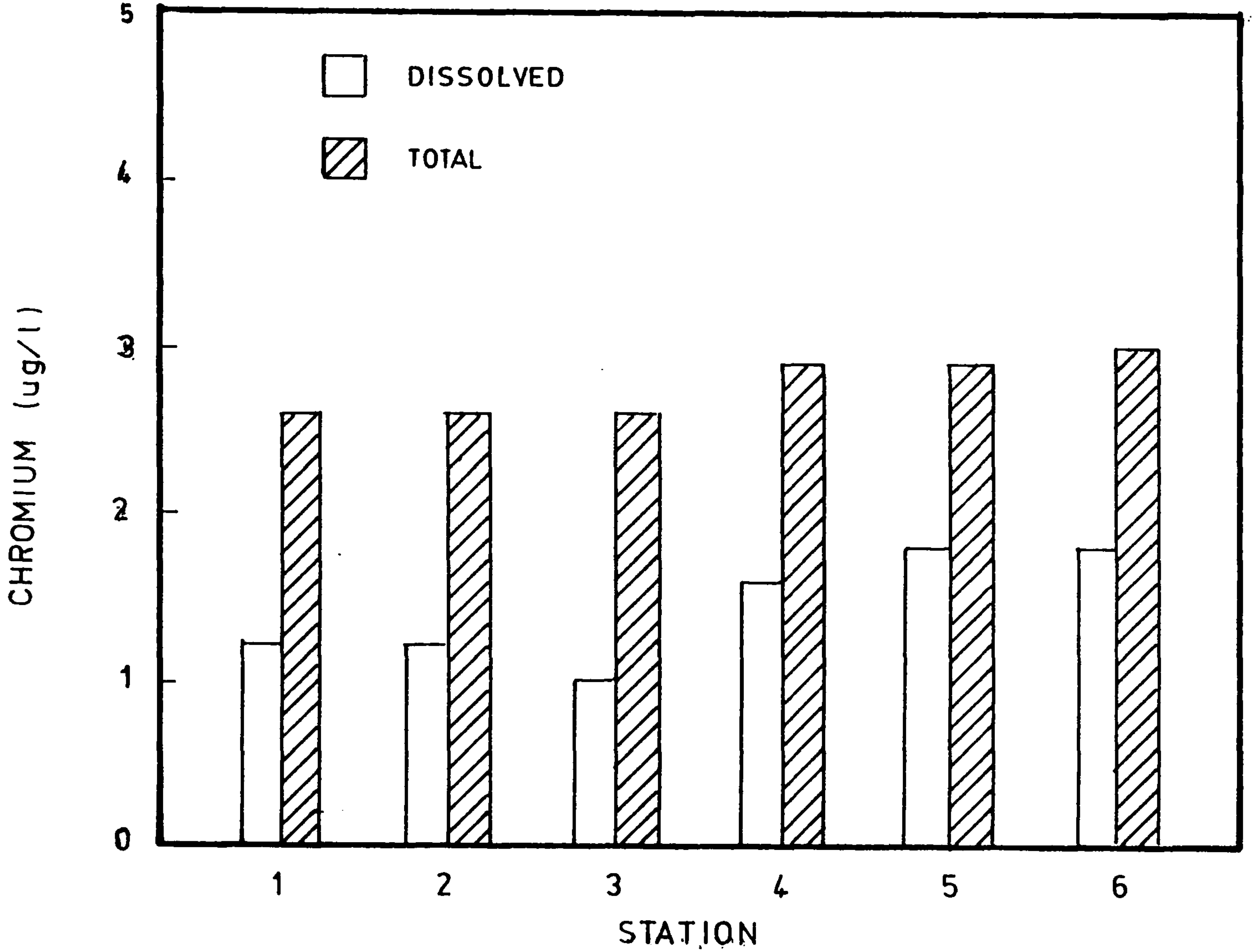


Figure 18. Total (unfiltered) and dissolved (filtered) chromium concentrations in water for all six Bull Run stream stations.

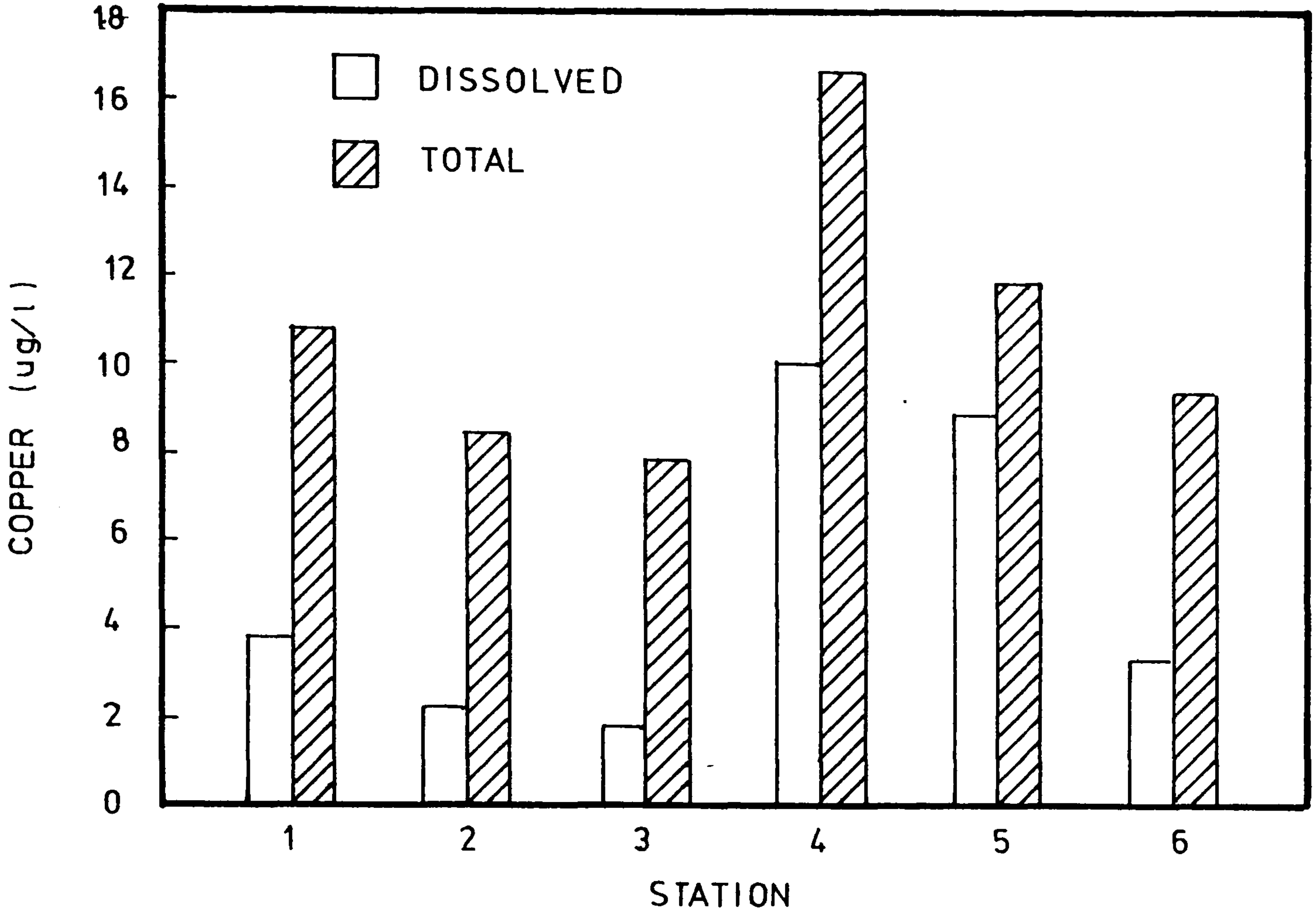


Figure 19. Total (unfiltered) and dissolved (filtered) copper concentrations in water for all six Bull Run stream stations.

total at all six stations. Dissolved Cr concentrations ranged from 33 percent of the total at Stations 1, 2, and 3 to 66 percent at Stations 4, 5, and 6. Dissolved Cu was lowest at Stations 1, 2, 3, and 6 (25 to 35 percent) and highest at Stations 4 and 5 (65 to 75 percent).

Sediment. Mean ratios of extractable metals in sediments to total metal concentrations in water are summarized in Table 11 by metal and stream station. Metal ratios are tabulated for each station because it was demonstrated by multivariate analysis of variance that, for some reason, the stream stations influenced these ratios. (Such was the case for the mean metal concentrations in all stream components that were ranked by Duncan's Multiple Range Test.) Table 11, therefore, presents these mean ratios for each metal by the six stream stations. No apparent discernible trend exists for these ratios as functions of downstream distance. Therefore, some factor other than upstream/downstream location (possibly sediment characteristics) have influenced these ratios. To compare these ratios with concentration factors for the other stream components, ratios of each metal at all six stations were averaged. These average ratios were as follows: Cd, 170; Ni, 284; Zn, 862; Cu, 879; Cr, 1,170; Pb, 1,648; Mn, 4,379; Fe, 11,621.

Other Stream Components. Metal concentration factors (the ratio of metal concentration in the stream component divided by the total metal concentration in water) for detritus, caddisflies, snails, and crayfish appear in Table 12. Multivariate analysis of variance on these concentration factors (unlike the ratios for sediment) demonstrated

Table 11

Ratios of Extractable Metals in Sediments to Total Metal Concentrations in Water for All Six Bull Run Stream Stations

Stream Station	Extractable Metals in Sediments/Total Metals in Water: Averages and Ranges							
	Fe	Mn	Ni	Pb	Cd	Zn	Cr	Cu
1	11,087	4,058	258	1,520	120	370	1,187	493
	5,102-18,847	2,751-15,260	50-533	725-2,833	100-200	236-652	733-2,600	173-840
2	19,630	7,174	274	1,172	160	370	1,801	760
	6,754-32,977	2,825-15,260	51-650	600-1,660	100-200	267-630	640-3,000	229-1,366
3	10,458	4,373	336	2,572	140	448	1,240	1,207
	4,217-16,546	3,270-6,056	33-1,000	918-6,250	100-200	208-643	750-2,600	335-1,720
4	13,167	7,089	474	2,115	260	922	1,135	1,025
	5,589-21,933	3,248-15,500	39-1,750	1,655-2,500	200-400	310-2,638	650-2,100	374-1,500
5	7,384	1,907	82	1,119	140	2,443	663	549
	3,294-9,850	939-2,820	41-153	940-1,250	100-200	242-10,800	533-850	288-733
6	7,821	1,674	280	1,387	200	617	992	1,346
	3,886-12,142	802-2,583	46-775	1,115-1,837	100-300	416-820	700-1,600	422-2,380

Table 12

Concentration Factors for All Metals by the Stream Components Detritus, Caddisflies, Snails, and Crayfish

Stream Component	Average and Range for Concentrations Factors[a]							
	Fe	Mn	Ni	Pb	Cd	Zn	Cr	Cu
Detritus	19,283	26,301	1,293	3,078	877	7,737	4,443	3,086
	5,485-57,522	8,518-60,294	124-8,950	1,314-8,200	200-1,800	1,447-123,000	1,500-16,200	713-6,720
Caddisflies	10,739	15,467	1,143	1,943	1,653	6,139	2,148	3,745
	4,531-23,057	4,625-37,826	74-5,150	511-4,133	1,000-3,700	2,617-19,125	625-6,100	995-6,375
Snails	3,050	3,597	473	867	1,480	3,639	997	18,292
	913-7,988	3,297-10,195	52-1,725	392-1,683	900-2,100	1,200-7,100	280-2,100	4,117-33,800
Crayfish	329	584	753	1,288	0	6,061	0	11,709
	67-901	116-1,671	0-3,800	118-5,042	0-0	1,595-79,200	0-0	2,104-35,000

[a] Defined as the ratio of metal concentration in the stream component to the total metal concentration in the water for a given date and stream station. Average concentration factors were obtained by considering all dates and stream stations.

that the stream stations did not have any influence on the value of the concentration factors. Therefore, average concentration factors for these components were computed for all six stations.

Table 13 summarizes the relative order that each stream component concentrated the eight metals based upon the concentration factors appearing in Tables 11 and 12. (One should understand that reporting concentration factors for all stream components does not imply that each stream component concentrated--or accumulated--metals by the same mechanism.) Note that sediment, detritus, and caddisflies concentrated Fe and Mn to a larger extent than the other metals. For these components, Cd and Ni were concentrated the least. Snails and crayfish, however, concentrated more Cu and Zn than any other metal. Snails concentrated Ni the least, while concentrations of Cd and Cr were zero in crayfish.

Stream Component Relationships for Metals

Lead and Copper.

Pb was accumulated by the stream components in the order: detritus > caddisflies > sediment > crayfish > snails > water. It can be seen from Tables 11 and 12 that these components, respectively, accumulated Pb 3,078, 1,943, 1,648, 1,288 and 867 times the total Pb concentration in the water column. Stream component relationships for Pb can be found by examining the linear correlation coefficients computed for the various stream components presented in Table 14. A linear relationship appears to have existed for Pb in caddisflies with dissolved Pb in water, Pb in sediment, and Pb in detritus. A linear

Table 13

Relative Order of Metal Concentration Factors for Sediment, Detritus, Caddisflies, Snails, and Crayfish

Component	Order of Metal Concentration Factors[a]
Sediment	Fe > Mn > Pb > Cr > Cu > Zn > Ni > Cd
Detritus	Mn > Fe > Zn > Cr > Cu > Pb > Ni > Cd
Caddisflies	Mn > Fe > Zn > Cu > Cr > Pb > Cd > Ni
Snails	Cu > Zn > Mn > Fe > Cd > Cr > Pb > Ni
Crayfish	Cu > Zn > Pb > Ni > Mn > Fe > Cd = Cr = 0

[a] $$\text{Metal Concentration Factor} = \frac{\text{Metal Concentration in Stream Component}}{\text{Total Metal Concentration in Water}}$$

Table 14

Correlation Coefficients Derived from Comparisons of Lead Concentrations Among the Various Stream Components

Component	Total Lead in Water	Dissolved Lead in Water	Sediment	Detritus	Caddisflies	Snails	Crayfish
Total Lead in Water	1.00 (29)	0.75** (29)	0.45* (29)	0.27 (29)	0.30 (17)	-0.62 (9)	-0.02 (29)
Dissolved Lead in Water	0.75** (29)	1.00 (29)	0.56** (29)	0.35 (29)	0.53* (17)	-0.33 (9)	0.02 (29)
Sediment	0.46* (29)	0.56** (29)	1.00 (29)	0.54** (29)	0.76** (17)	-0.29 (9)	-0.02 (29)
Detritus	0.27 (29)	0.35 (29)	0.54** (29)	1.00 (29)	0.74** (17)	0.03 (9)	0.26 (29)
Caddisflies	0.30 (17)	0.53* (17)	0.76** (17)	0.74** (17)	1.00 (17)	0.02 (7)	0.10 (17)
Snails	-0.62 (9)	-0.33 (9)	-0.29 (9)	0.03 (9)	0.02 (7)	1.00 (9)	0.20 (7)
Crayfish	-0.02 (29)	0.02 (29)	-0.02 (29)	0.26 (29)	0.10 (17)	0.20 (7)	1.00 (29)

*Significant at 0.95 Confidence Level. **Significant at 0.99 Confidence Level

( ) Number of Observations.

relationship between Pb in detritus and sediment is also suggested. Furthermore, there appears to have been a linear relationship for Pb in sediment with total and dissolved Pb in water. A linear relationship also appears to have existed between total and dissolved Pb in water.

Cu was accumulated by the stream components in the order: snails > crayfish > caddisflies > detritus > sediment > water. It can be seen from Tables 11 and 12 that these components, respectively, accumulated Cu 18,292, 11,709, 3,745, 3,086, and 897 times the total Cu concentration in water. Stream component relationships for Cu can be found by examining the linear correlation coefficients computed for the various stream components presented in Table 15. A linear relationship appears to have existed for Cu in crayfish with dissolved Cu in water, and Cu in sediment, detritus, and caddisflies. A linear relationship is also suggested between Cu in snails and sediment. Additionally, a linear relationship appears to have existed for Cu in caddisflies with total and dissolved Cu in water, Cu in sediment, and Cu in detritus. Cu in detritus also appears to have been related to total and dissolved Cu in water, and Cu in sediment. Additionally, a linear relationship also appears to have existed between total and dissolved Cu in water.

Other Metals. From Table 16, one can see the order of affinity the stream components exhibited for concentrating the various metals. Generally, detritus and caddisflies concentrated the metals Mn, Ni,

Table 15

Correlation Coefficients Derived from Comparisons of Copper Concentrations Among the Various Stream Components

Component	Total Copper in Water	Dissolved Copper in Water	Sediment	Detritus	Caddisflies	Snails	Crayfish
Total Copper in Water	1.00 (29)	0.51** (29)	0.46* (29)	0.52** (29)	0.74** (17)	-0.23 (9)	0.34 (29)
Dissolved Copper in Water	0.51** (29)	1.00 (29)	0.65** (29)	0.74** (29)	0.86** (17)	0.55 (9)	0.69** (29)
Sediment	0.46* (29)	0.65** (29)	1.00 (29)	0.69** (29)	0.93** (17)	0.81** (9)	0.59** (29)
Detritus	0.52** (29)	0.74** (29)	0.69** (29)	1.00 (29)	0.90** (17)	0.43 (9)	0.73** (29)
Caddisflies	0.74** (17)	0.86** (17)	0.93** (17)	0.90** (17)	1.00 (17)	0.49 (7)	0.92** (17)
Snails	-0.23 (9)	0.55 (9)	0.81** (9)	0.43 (9)	0.49 (7)	1.00 (9)	0.54 (9)
Crayfish	0.34 (29)	0.69** (29)	0.59** (29)	0.73** (29)	0.92** (17)	0.54 (9)	1.00 (29)

*Significant at the 0.95 Confidence Level. **Significant at the 0.99 Confidence Level.

( ) Number of observations.

Table 16

The Order of Affinity by the Stream Components for Each Metal

Metal	Order by which the Stream Components Concentrated[*] A Metal
Fe	Detritus > Sediment > Caddisflies > Snails > Crayfish
Mn	Detritus > Caddisflies > Sediment > Snails > Crayfish
Ni	Detritus > Caddisflies > Crayfish > Snails > Sediment
Pb	Detritus > Caddisflies > Sediment > Crayfish > Snails
Cd[**]	Caddisflies > Snails > Detritus > Sediment
Zn	Detritus > Caddisflies > Crayfish > Snails > Sediment
Cr[**]	Detritus > Caddisflies > Sediment > Snails
Cu	Snails > Crayfish > Caddisflies > Detritus > Sediment

[*] Based upon concentration factors.

[**] Cd and Cr concentrations were zero in crayfish.

Pb, Zn, and Cr greater than the other stream components. Snails and crayfish generally concentrated these metals less than the other stream components. Snails and crayfish concentrated Cu greater than the other stream components, however.

Correlation coefficients among the stream components for Fe, Mn, Ni, Cd, Zn, and Cr appear in Appendix Tables F1 through F6. These metals did not show nearly as many relationships as did Pb and Cu. No significant relationships could be found for Cd. Correlation coefficients among stream components for some metals (Fe, Ni, Cr) were negative. Significant relationships, however, were found for dissolved Fe in water with Fe in crayfish and total Fe in water; Mn in sediment with Mn in snails, and total Mn with dissolved Mn in water; and Zn in snails with Zn in detritus.

V. DISCUSSION

Variation of Metal Concentrations with Downstream Distance

The results demonstrated that both Pb and Cu were accumulated by a majority of the stream components. Additionally, downstream variations in concentrations of both these metals different from those of any other metals studied. As noted earlier, mean Pb and Cu concentrations within most stream components were greater at the stations downstream of Flat Branch (Stations 4, 5, and 6) than at the upstream stations (1, 2, and 3). This general statement cannot be made concerning observed variations for the other metals. Furthermore, when Stations 1, 4, and 6 are compared, Pb and Cu concentrations followed a definite trend that did not exist for concentrations of the other metals.

Figures 20 through 27 are summaries of data presented in the previous section and show mean metal concentrations in water, sediment, detritus, caddisflies, and crayfish at Stations 1, 4, and 6. These stations were chosen for discussion because they represent the most upstream and downstream stations (1 and 6, respectively) in relation to the first station (4) on Bull Run that was located immediately downstream of Flat Branch, the major stormwater source input to Bull Run. If heavy metals present in urban runoff are accumulated in a stream, then these metals should accumulate in stream components at greater concentrations immediately below the runoff input than farther downstream or upstream of the input source. Therefore, the metals that accumulated in stream components to the greatest extent at Station 4 than at Stations

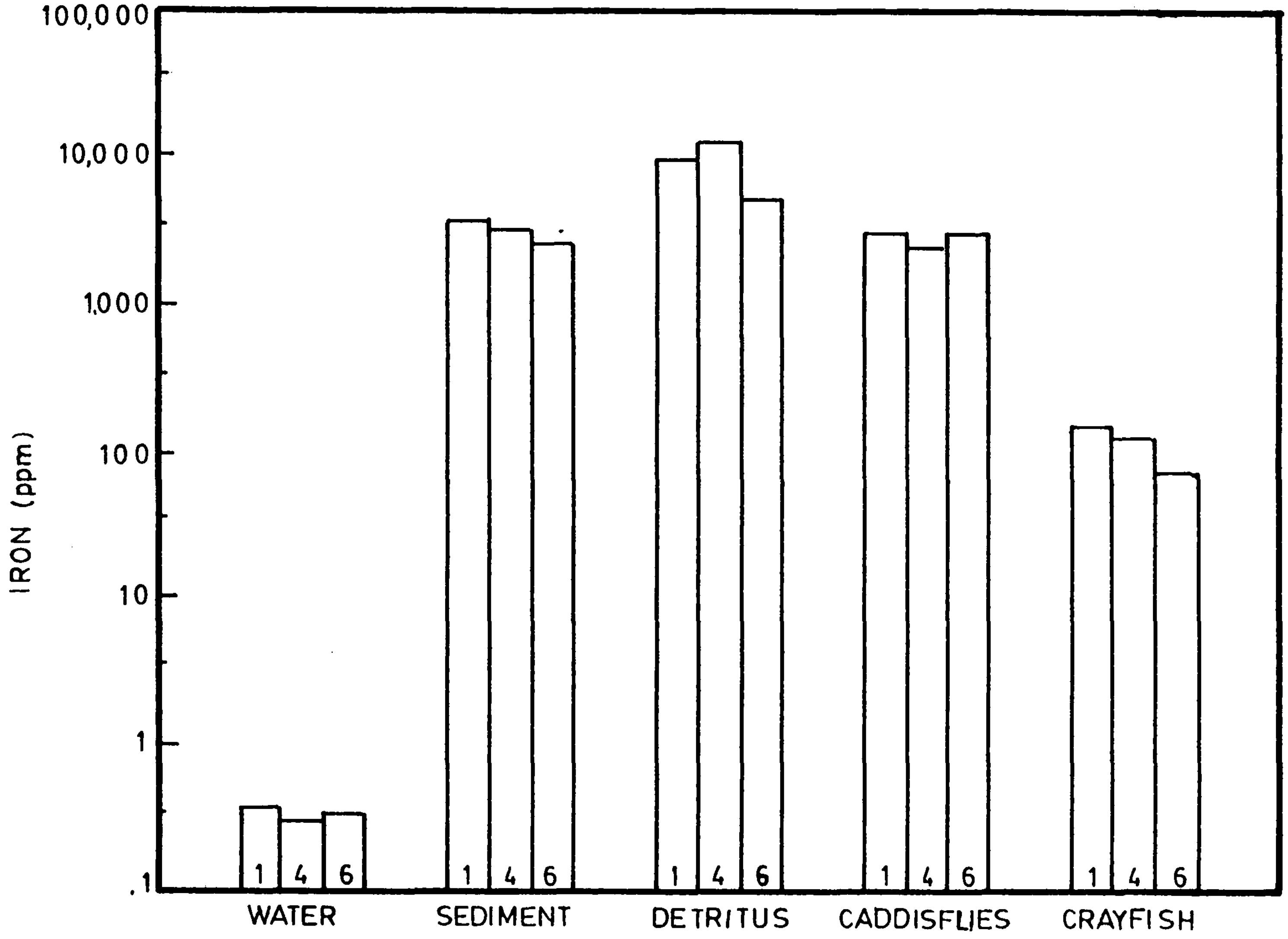


Figure 20. Comparisons of iron concentrations instream components at Stations 1, 4, and 6.

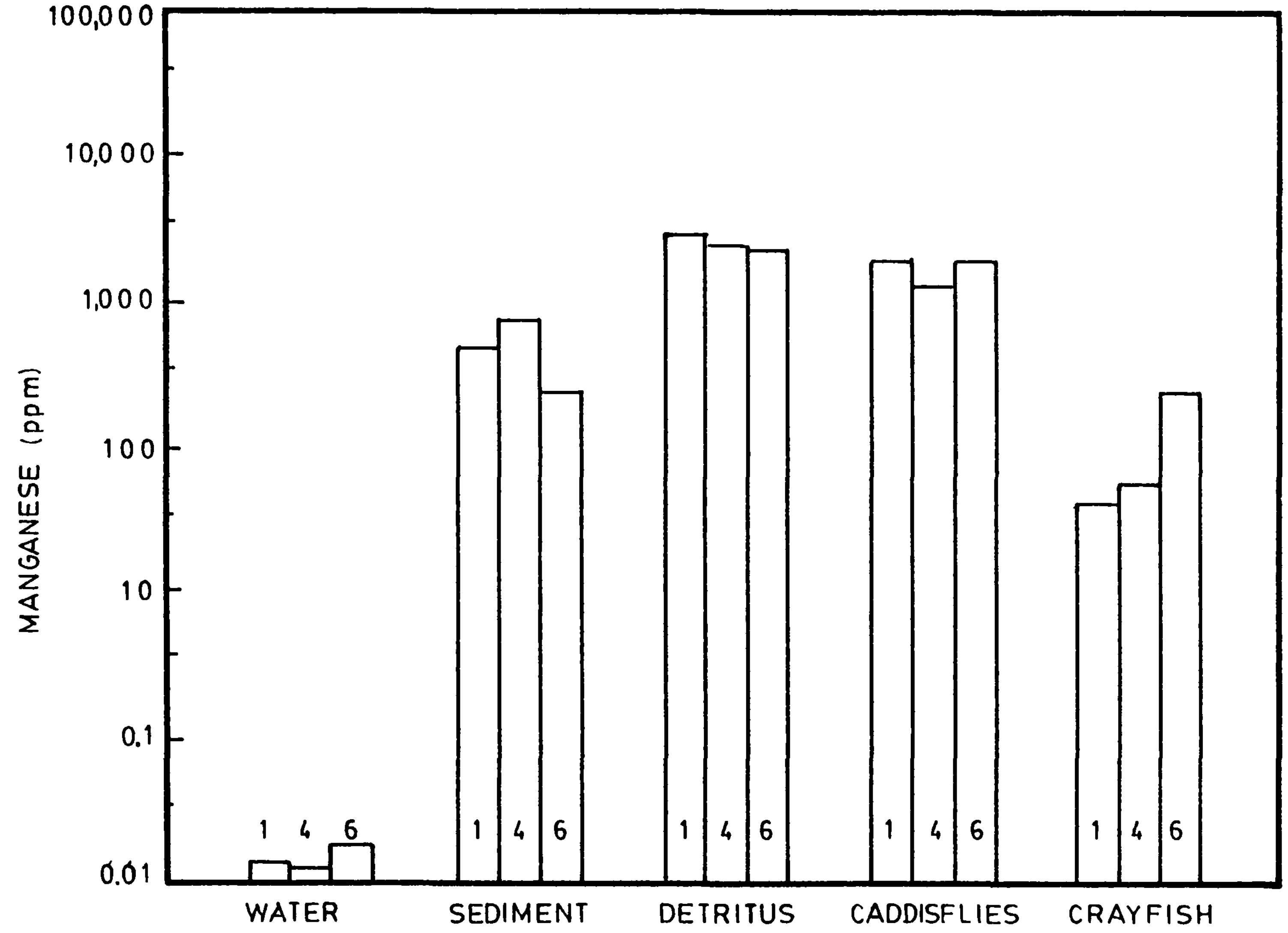


Figure 21. Comparisons of manganese concentrations in stream components at Stations 1, 4, and 6.

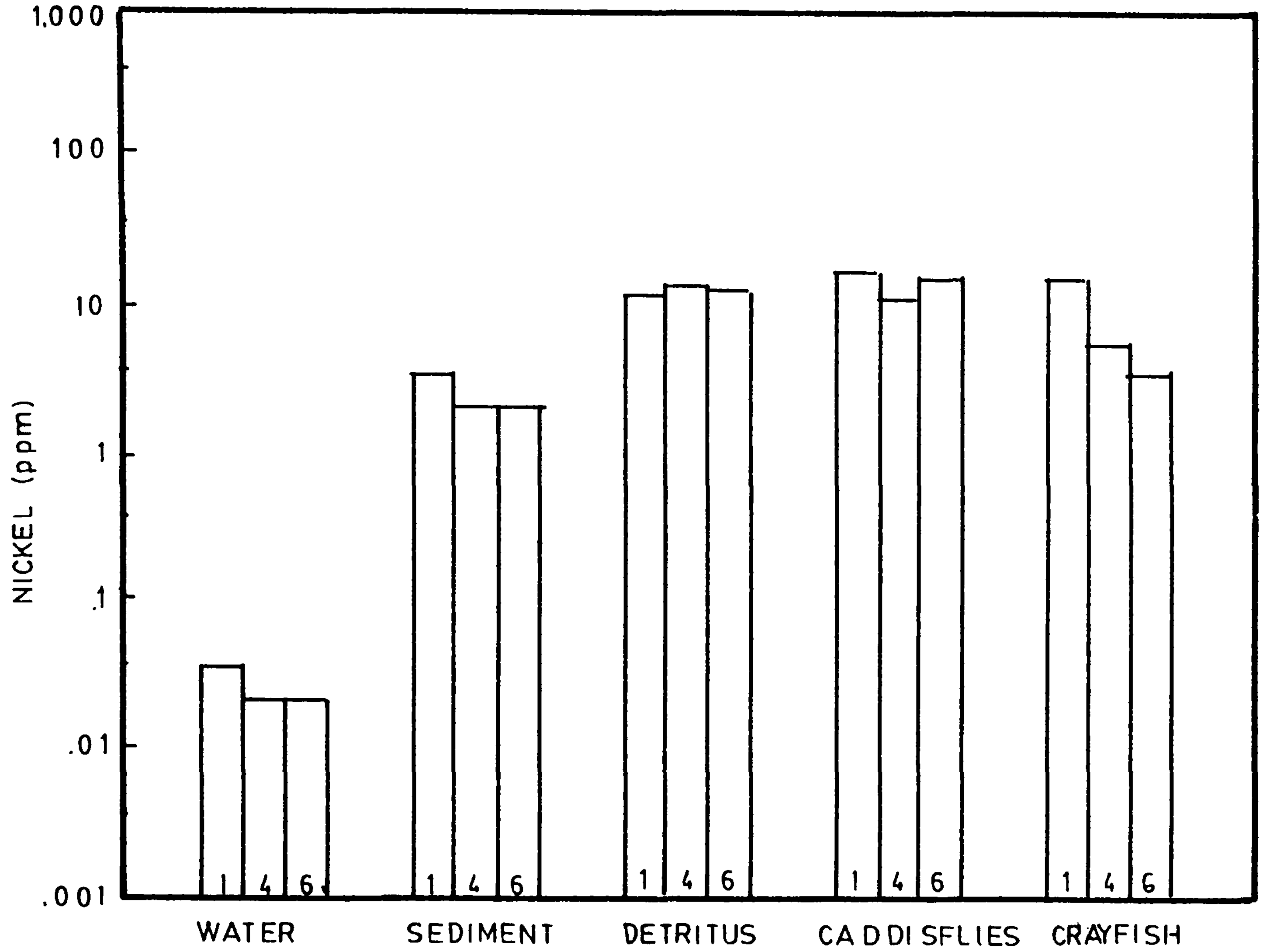


Figure 22. Comparisons of nickel concentrations in stream components at Stations 1, 4, and 6.

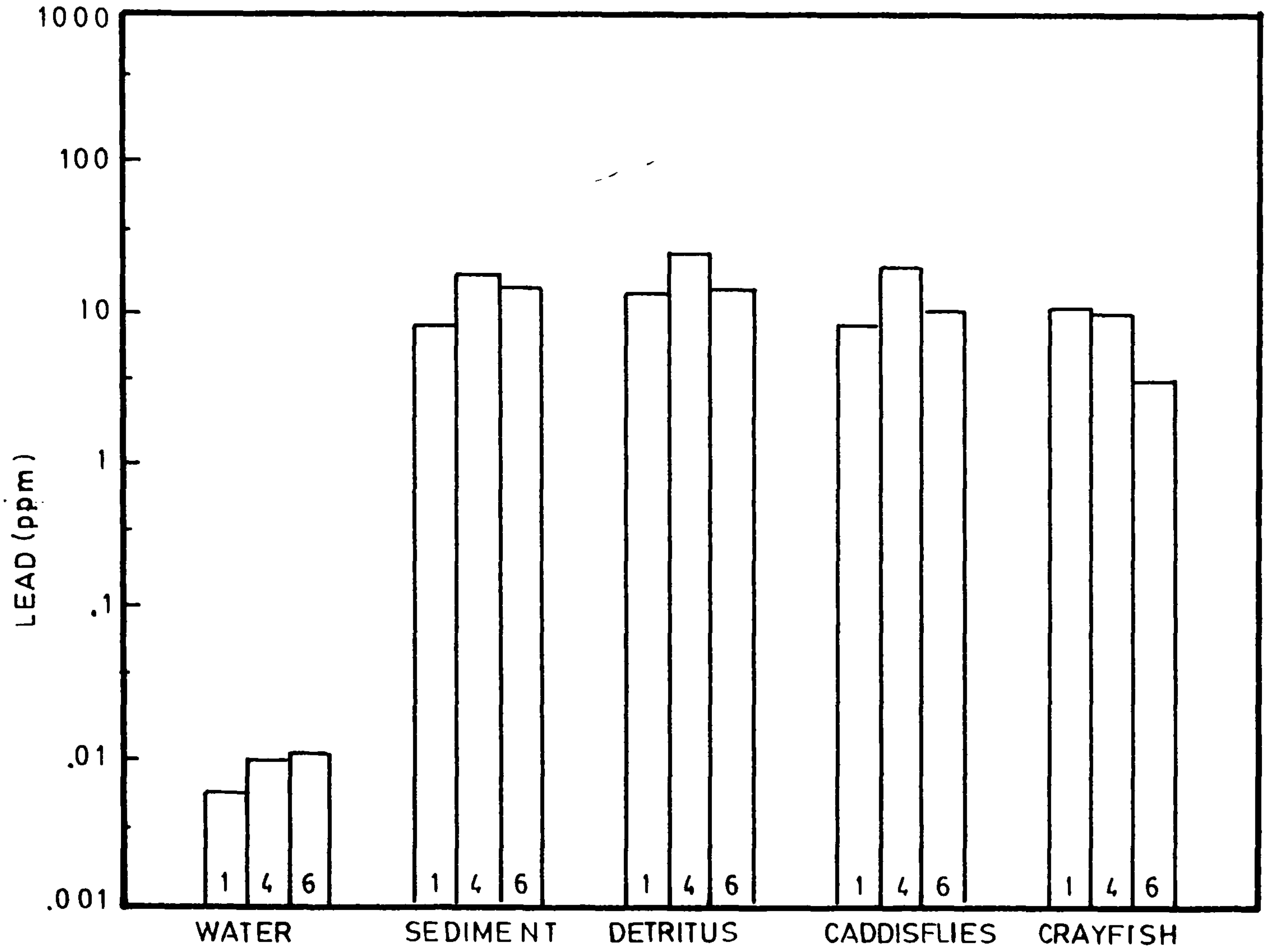


Figure 23. Comparisons of lead concentrations in stream components at Stations 1, 4, and 6.

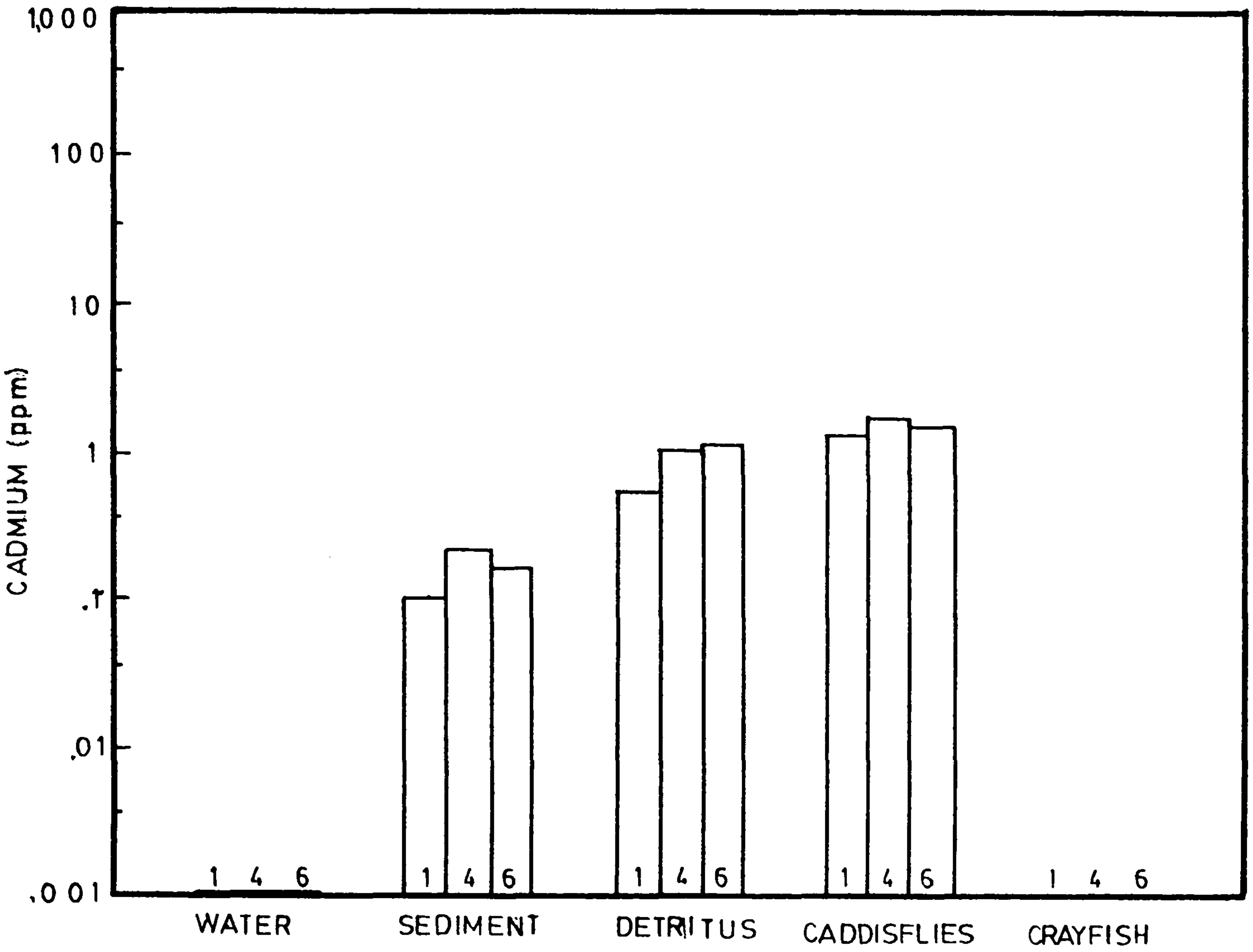


Figure 24. Comparisons of cadmium concentrations in stream components at Stations 1, 4 and 6.

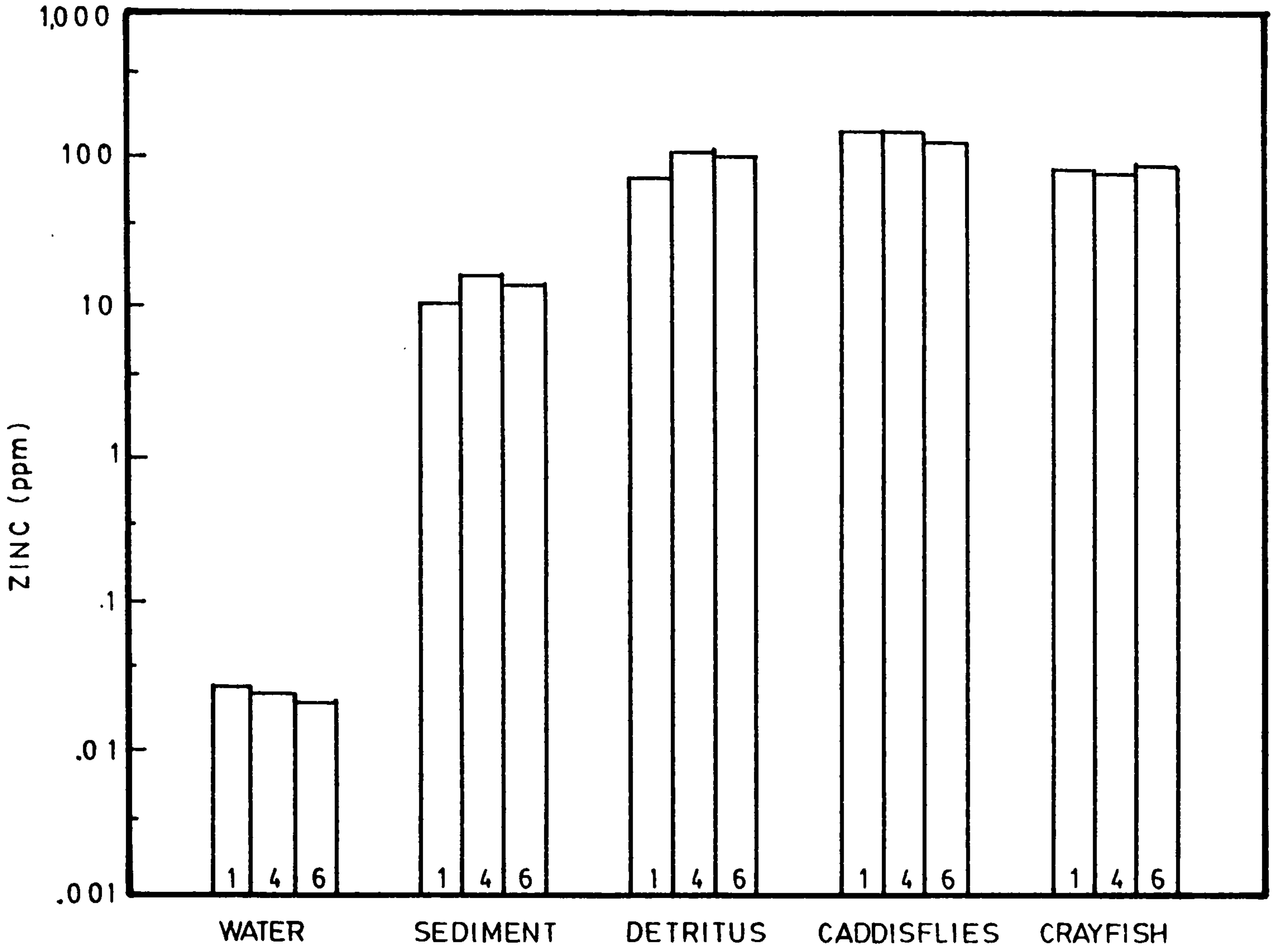


Figure 25. Comparisons of zinc concentrations in stream components at Stations 1, 4, and 6.

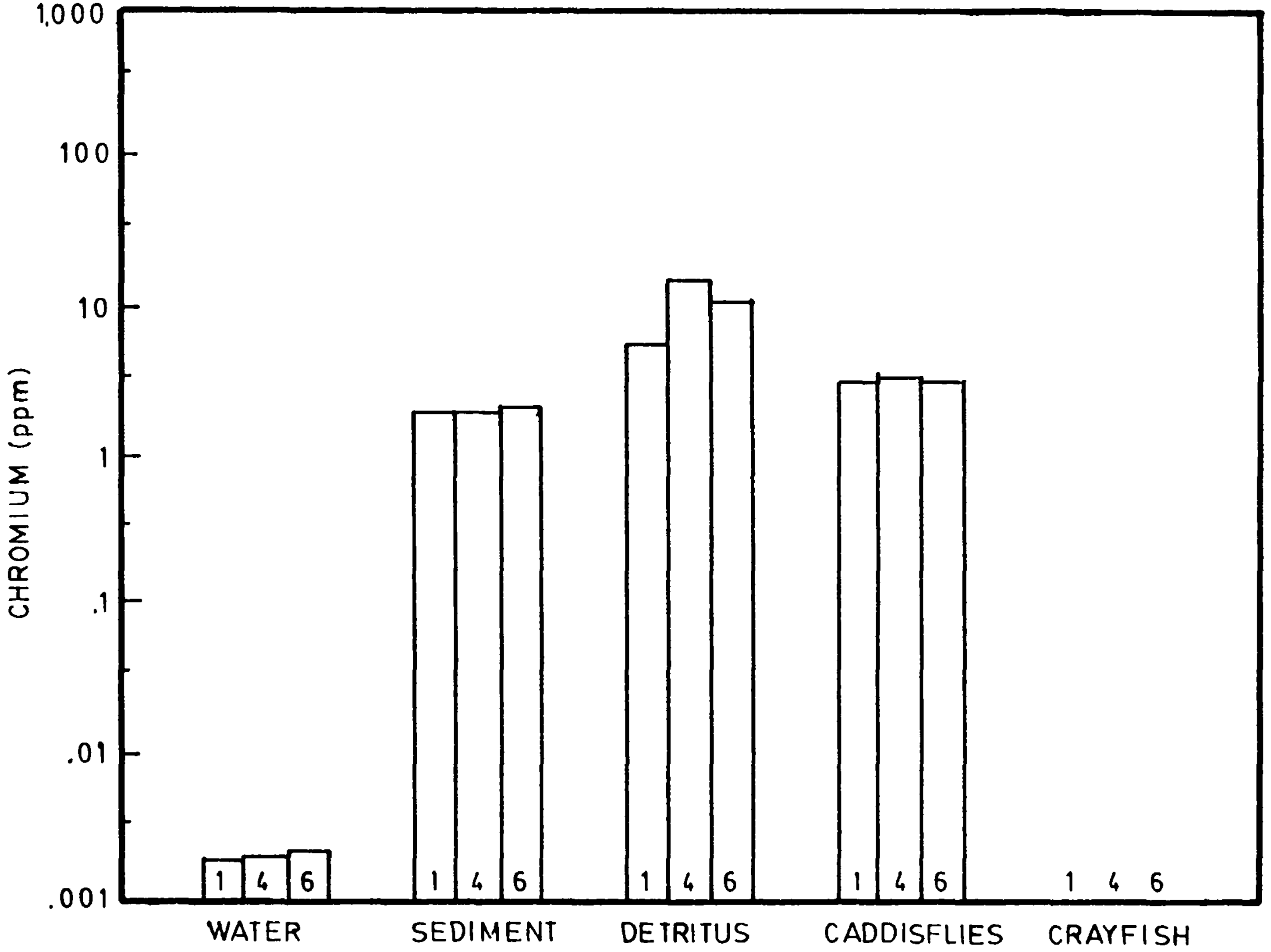


Figure 26. Comparisons of chromium concentrations in stream components at Stations 1, 4, and 6.

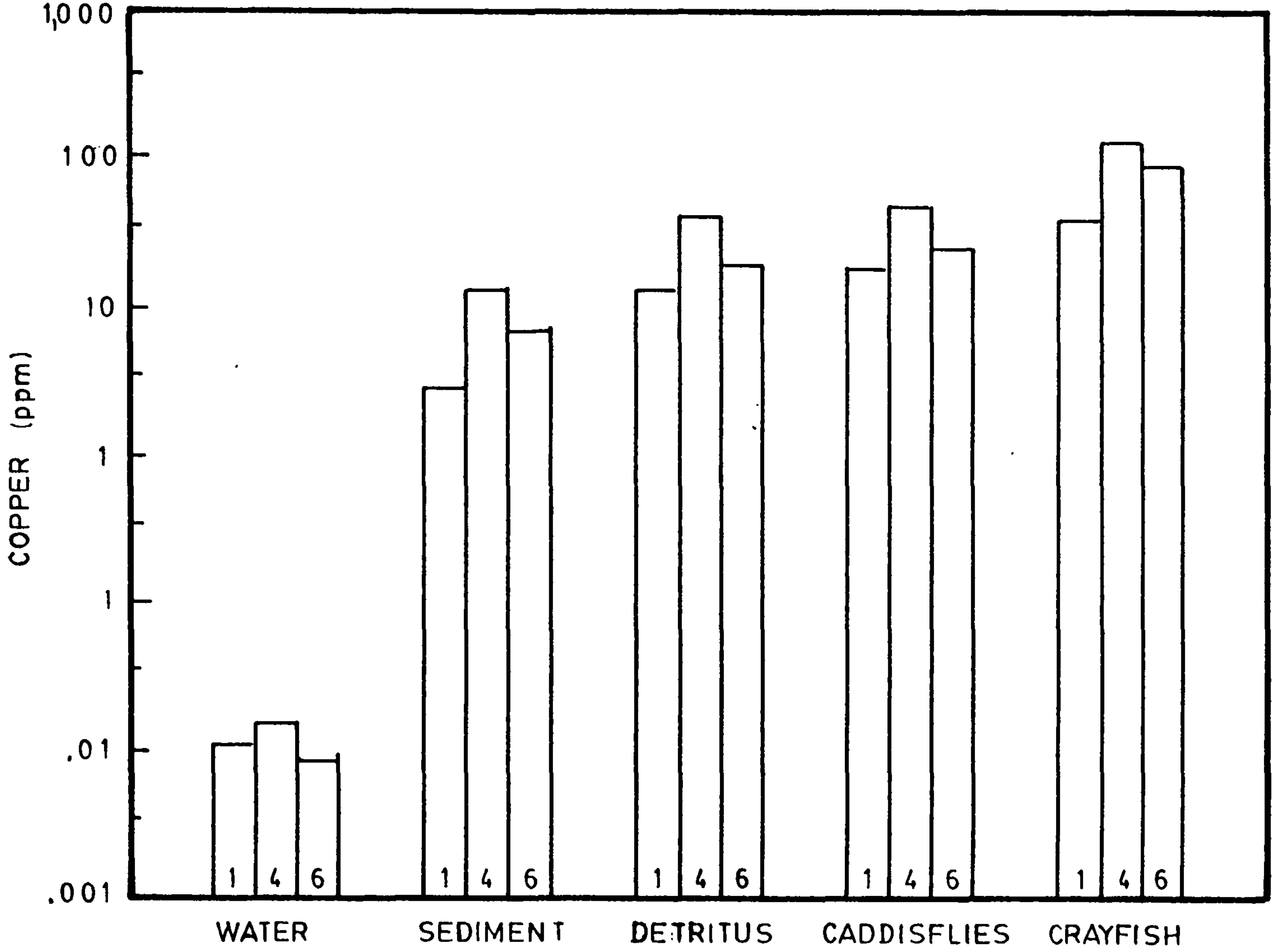


Figure 27. Comparisons of copper concentrations in stream components at Stations 1, 4, and 6.

1 and 6 probably were derived more from urban runoff than any other source.

From Figures 20 through 27, Pb and Cu exhibited the highest mean metal concentrations in sediment, detritus, and caddisflies at Station 4 than at Stations 1 and 6. Additionally, mean Pb and Cu concentrations for these components were greater at Station 6 than Station 1. No other metal exhibited this trend for these three stream components. Concentrations of Cu in crayfish also followed this trend. Mean total Pb and Cu concentrations in water were also greater at Station 4 than at Station 1. Thus, Pb and Cu concentrations in a majority of stream components were greatest immediately downstream of the urban stormwater input from Flat Branch. When examining Figures 20 through 27, the reader should take note that the ordinate is a log scale. The actual differences in concentrations are not as obvious as they would be if the scale was arithmetic. The purpose of displaying data on a log scale, however, was to ensure that all components could be shown on the same graph.

Metals other than Pb and Cu were accumulated in some stream components at Station 4 to a greater degree than Station 1: sediment accumulated more Mn, Cd, and Zn; detritus, more Fe, Ni, Cd, Zn, and Cr; caddisflies, more Cd, Zn, and Cr; and crayfish, more Mn. Although some stream components accumulated greater amounts of a metal at Station 4 than at Station 1, no other metal was accumulated to a greater extent by as many stream components as were Pb and Cu.

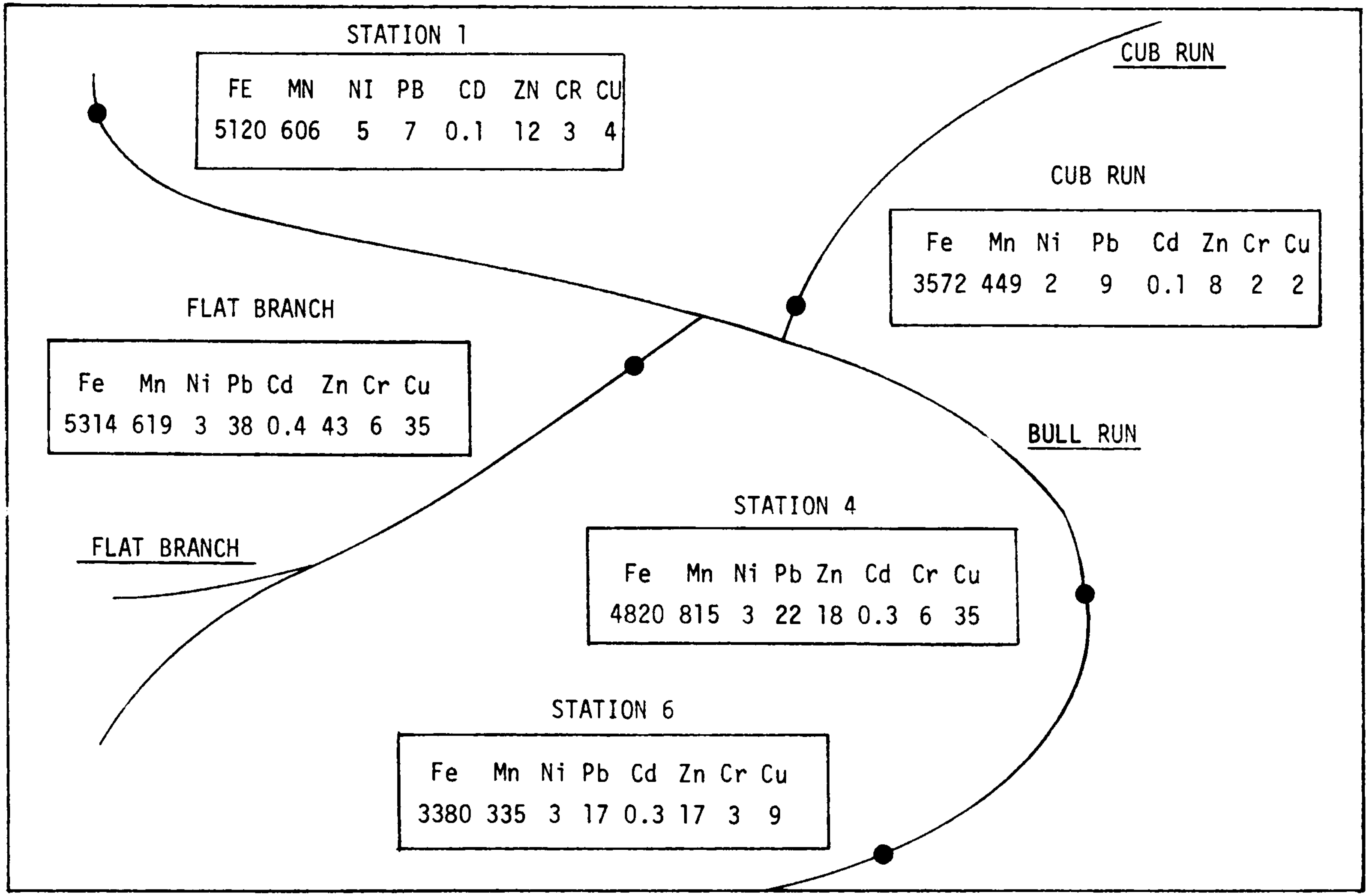
Because Flat Branch and Cub Run empty into Bull Run upstream of Station 4, sediment samples were also obtained from these tributaries on three separate occasions so that the metal concentrations and other characterizing data could be determined. Table 17 presents average and ranges of extractable metals for these sediments. Figure 28 shows metal contents for these sediments and sediments from Stations 1, 4, and 6. Although concentrations of all metals in Flat Branch sediments were greater than those in Cub Run sediments, concentrations of Pb, Zn, Cd, Cr, and Cu were particularly greater. These concentrations were, respectively, 4.2, 4.0, 5.4, 3.0, and 17.5 times greater in Flat Branch than in Cub Run. Fe, Mn, and Ni in Flat Branch sediments were only 1.5, 1.4, and 1.5 times greater. Moreover, sediment Fe and Mn concentrations were similar at both Station 1 and at Flat Branch, while Ni was higher in sediments at Station 1 than at Flat Branch. It appears from these data that urban stormwater flowing through Flat Branch has contributed Pb, Cu, and possibly Cd, Zn, and Cr to Bull Run.

Mean extractable Cd and Zn concentrations in sediments were significantly greater at Station 4 than at Station 1 (Appendix Tables E4 and E5), while mean extractable Cr in sediments at Stations 1 and 4 were not found to be significantly different (Appendix Table E6). Unlike Pb and Cu, however, Cd and Zn were not found to accumulate in any stream component other than sediment at concentrations significantly greater at Station 4 than at Station 1. Therefore, even though Flat Branch stormwater may have carried large quantities of Pb, Cu, Zn, Cd, and Cr from the Manassas and Manassas Park areas, only Pb and Cu

Table 17

Extractable Metals from Flat Branch and Cub Run Sediments
(average and range)

Location	Extractable Metals, µg/g							
	Fe	Mn	Ni	Pb	Cd	Zn	Cr	Cu
Flat Branch	5,310	619	3	38	0.4	43	6	35
	5,230 - 5,530	530 - 735	3 - 3	36 - 42	0.3 - 0.4	36 - 48	6 - 7	16 - 55
Cub Run	3,570	449	2	9	0.1	8	2	2
	2,970 - 4,140	398 - 492	2 - 3	7 - 10	0.1 - 0.1	7 - 9	2 - 3	2 - 3



STATION 1

FE	MN	NI	PB	CD	ZN	CR	CU
5120	606	5	7	0.1	12	3	4

CUB RUN

Fe	Mn	Ni	Pb	Cd	Zn	Cr	Cu
3572	449	2	9	0.1	8	2	2

FLAT BRANCH

Fe	Mn	Ni	Pb	Cd	Zn	Cr	Cu
5314	619	3	38	0.4	43	6	35

STATION 4

Fe	Mn	Ni	Pb	Zn	Cd	Cr	Cu
4820	815	3	22	18	0.3	6	35

STATION 6

Fe	Mn	Ni	Pb	Cd	Zn	Cr	Cu
3380	335	3	17	0.3	17	3	9

Figure 28. Metal concentrations in sediment at Bull Run Stations 1, 4, and 6 and at Flat Branch and Cub Run.

were accumulated by a majority of Bull Run stream components below the source of urban stormwater.

Relative Metal Accumulation for Stream Components

Water. All metals (dissolved and total) found in Bull Run were in concentrations far below levels that would warrant a public health concern. Table 18 summarizes the United States Public Health Service drinking water standards (65) and EPA's water quality criteria for the metals studied (66).

Iron is the fourth most abundant element that makes up the earth's crust and is an important constituent of soils and clays. It is found in the ore hematite (Fe_2O_3) and the mineral magnetite which is seen as black sand on beaches and stream banks (67). Iron is also an important trace element required by both plants and animals. For industrial and domestic use, iron can become objectionable because of taste and staining problems when present in concentrations greater than 0.3 mg/l. In freshwater aquatic systems, Fe concentrations greater than 1.0 mg/l may be toxic to trout and other fish (66).

In the present study, total Fe concentrations in water were well below the 1.0 mg/l criterion set by EPA for the protection of freshwater aquatic life. Warnick and Bell (45) found the 96-hour LC_{50} for the mayfly *Ephemerella subvaria* to be 0.32 mg/l Fe^{++}. In the same study, 50 percent of the caddisflies *Hydropsyche betteni* survived for 7 days in water containing 16.0 mg/l Fe^{++}. Dissolved Fe concentrations (iron passing through a glass-fiber filter) in Bull Run averaged from

Table 18

USPHS Drinking Water Standards and Water Quality Criteria for Metals Concentration in Water

Metal	USPHS Drinking Water Standard* mg/l	EPA Water Quality Criteria**
Iron	0.30	0.3 mg/l for domestic water supplies. 1.0 mg/l for freshwater aquatic life.
Manganese	0.05	0.05 mg/l for domestic water supplies. 0.1 mg/l for protection of consumers of marine mollusks.
Nickel	--	0.01 times the 96-hour LC_{50} for freshwater and marine aquatic life.
Lead	0.05	0.05 mg/l for domestic water supplies. 0.01 times the 96-hour LC_{50} value, using the receiving or comparable water as the dilutent and soluble lead measurements (using an 0.45 micron filter), for sensitive freshwater resident species.
Cadmium	0.01	0.01 mg/l for domestic water supplies. 0.4 µg/l (softwater), 1.2 µg/l (hard water) for cladocerans and salmonid fishes. 4.0 µg/l (soft water), 12.0 µg/l (hard water) for other less sensitive, aquatic life.

Table 18 (Continued)

Metal	USPHS Drinking Water Standard* mg/l	EPA Water Quality Criteria**
Zinc	5.00	5.0 mg/l for domestic water supplies. 0.01 of the 96-hour LC_{50} as determined through bioassay using a sensitive fresh-water resident species.
Chromium	0.05***	0.05 mg/l for domestic water supplies. 0.1 mg/l for freshwater aquatic life.
Copper	1.00	1.0 mg/l for domestic water supplies. 0.1 times the 96-hour LC_{50} as determined through non-aerated bioassay using a sensitive freshwater or marine aquatic resident species

* (65)
** (66)
*** Hexavalent Chromium

116 to 180 μg/l. Therefore, Fe concentrations in water pose no danger to freshwater aquatic organisms in Bull Run.

Manganese, frequently associated with Fe compounds, usually occurs in oxide, silicate, and carbonate minerals. A vital micro-nutrient for both plants and animals, Mn is thought to be essential for the utilization of Vitamin B_1 by animals. (67). It can cause taste and staining problems, even more objectionable than Fe, when in concentrations greater than 0.05 mg/l. Since Mn ions are rarely found at concentrations greater than 1 mg/l and tolerance values reported for freshwater aquatic life range from 1.5 mg/l to over 1000 mg/l, Mn is not considered to be a problem in freshwaters (66).

Dissolved mean Mn concentrations in Bull Run were found to be as high as 161 μg/l. This value is 3.2 times higher than the 50 μg/l limit set by the USPHS for domestic water supplies. With adequate water treatment practices, however, Mn should not cause any concern for the public's welfare.

The principal source of Ni in the environment is the weathering of ultramafic rocks. Most Ni is used in alloys to make a wide variety of consumer goods. Nickel is also present in Ni-Cd batteries, asbestos processing, and diesel engine exhausts (68). It is obtained commercially from pentlandite and pyrrhotite (67). Nickel salts are highly soluble in water and occur as leachate from Ni-bearing ores. For the most part, Ni is relatively less toxic to fish than other metals, and is usually considered to be relatively nontoxic to man (66).

In the present study, total Ni concentrations were found to be as high as 106 µg/l. However, concentrations usually averaged 20 to 40 µg/l. Warnick and Bell (45) found the 96-hour LC_{50} for the mayfly Ephemeralla subvaria and the stonefly Acroneuria lycorias to be 4.0 and 33.5 mg/l Ni^{++}, respectively. At a concentration of 64.0 mg/l Ni^{++}, 50 percent of the caddisflies Hydropsyche betteni survived for more than 14 days. Rehwoldt et al. (46) found static bioassay 96-hour LC_{50} values for an unidentified caddisfly and the snail Amnicola sp. to be 21.2 and 11.4 mg/l, respectively. Pickering et al. (69) found the 96-hour TL_{50} for the fathead minnow (Pimephales promelas) to be 27 mg/l. Thus, Ni concentrations found in Bull Run should pose no problems to aquatic organisms.

Commercially, Pb is obtained chiefly from galena (PbS). Other common forms include cerrusite ($PbCO_3$), anglesite ($PbSO_4$) and minim (Pb_3O_4). Lead is a common constituent of gasoline, paints, and pipes (67). Precipitation, municipal and industrial wastes, and urban runoff introduce Pb into the aquatic environment. It has no known beneficial or desirable nutritional effect and may tend to accumulate in the tissues of man and other animals (66).

Lead concentrations found in Bull Run water were far below the USPHS 50 µg/l standard. Thus lead concentrations in Bull Run do not warrant any public health concern. Warnick and Bell (45) found the 7-day LC_{50} for the caddisfly Hydropsyche betteni and the mayfly Ephemerella subvaria to be 32.0 and 16.0 mg/l, respectively. Biesinger and Christensen (70) found the 48-hour LC_{50} for the water flea, Daphnia magna to be

0.45 mg/l. Pickering et al. (69) found the 96-hour LC_{50} (20 mg/l hardness) to be 55.8 mg/l for the fathead minnow (Pimephales promelas) and 23.8 mg/l for the bluegill sunfish (Lepomis macrochirus). Thus, lead in water should not pose any problems to aquatic organisms in Bull Run.

Frequently associated with Zn and Pb ores, Cd occurs chiefly as the sulfide salt, greenockite (67). Friberg et al.(71) stated that no naturally occurring material will be completely free from Cd. It enters the environment through mining, smelting, and burning of oil and waste scrap material (71). Cadmium is accumulated in the liver and kidneys of man and was responsible for the occurrence of itai-itai disease which resulted in the death of approximately 100 Japanese between 1940 and 1965 (66, 72). Presently, there is no known physiological need for Cd.

Cadmium concentrations found in Bull Run (1 μg/l) exceeded the 0.4 μg/l criterion for soft water (less than 75 mg/l $CaCO_3$) set by EPA for cladocerans, but was less than the limit (12 μg/l) for protecting aquatic life in hard water. Cadmium concentrations found in Bull Run were one-tenth the primary drinking water standard set by the USPHS. The 10-day static LC_{50} (56 mg/l hardness) for the caddisfly Hydropsyche betteni was found to be 32.0 mg/l (46). The midge, Tanytarsus dissimilis, has been found to be one of the most sensitive invertebrate tested, the 10-day LC_{50} (45-66 mg/l hardness) being 3.4 μg/l [66]. Pickering and Gast (73) reported a 96-hour flow-through LC_{50} (200 mg/l hardness) for the fathead minnow (Pimephales promelas) of 2.0 mg/l. Thus, with the exception of sensitive zooplankton, Cd concentrations pose no threat to aquatic organisms in Bull Run.

Zinc, often associated with the sulfides of Pb, Cu, Cd, and Fe, is found in nature predominantly as the sulfide, sphalerite (67). The metal is used in galvanizing, preparation of alloys, production of chemical products, and photoengraving. Zinc is an essential and beneficial element in human metabolism. However, excessive amounts have caused degeneration of the heart endocardium, congestion of the lungs, and damage to the liver, spleen, and brain, as well as death (66).

Zinc concentrations in water in Bull Run were far below the 5.0 mg/l USPHS drinking water standard. For the fathead minnow, Pimephales promelas, the 96-hour static LC_{50} was 780 μg/l (20 mg/l hardness)(69). Rehwoldt et al. (46) determined the 96-hour static LC_{50} for an unidentified caddisfly to be 58.1 mg/l (50 mg/l hardness). Using the fathead minnow as a sensitive species, the criterion, as set by EPA, would then become 7.8 μg/l. Total zinc concentrations averaged from 24 to 36 μg/l in Bull Run.

Chromium usually is found in its principal ore, chromite ($FeO \cdot Cr_2O_3$)(67). It can exist in several valance states, generally 2, 3, and 6. In the aquatic environment, Cr usually exists in either the trivalent or hexavalent form. Hexavalent Cr is a strong oxidizing agent and is generally more toxic than trivalent Cr. Trivalent Cr is an essential trace element for humans, whereas hexavalent Cr is harmful causing skin disorders, lung cancer, and other respiratory complications (66).

Total Cr concentrations averaged 3 μg/l in Bull Run. Since the pH was well above 5.0, it is most likely that all Cr was in the hexavalent form (66). Even so, this value is greatly below the 50 μg/l USPHS standard for hexavalent Cr. Warnick and Bell (45) found the 96-hour static LC_{50} for the mayfly _Ephemerella_ _subvaria_ and the caddisfly _Hydropsyche_ _betteni_ to be 2.0 mg/l Cr^{+++} (50 mg/l hardness) and 64.0 mg/l Cr^{+++} (46 mg/l hardness), respectively. Pickering and Henderson (69) tested four species of fish in softwater (20 mg/l $CaCO_3$) and found trivalent Cr to be more toxic to fishes than the hexavalent form. For the fathead minnow, _Pimephales_ _promelas_, 96-hour LC_{50} values (20 mg/l hardness) were 5.07 mg/l using trivalent Cr and 17.6 mg/l using hexavalent Cr. Thus, Cr in water should pose no problem to aquatic life in Bull Run.

Copper has been known to man and has been used for a variety of products since prehistoric times. It occurs in nature as a sulfide (bromite), an oxide (malachite), or a carbonate (cuprite). The electrical industry is one of the greatest users of Cu (67). It is frequently incorporated into paint and wood preservatives to inhibit algal growth. Oxides and sulfates of Cu are used for pesticides, algicides, and fungicides. Copper is also an important trace element for humans as well as other forms of life. In some invertebrate organisms, Cu is incorporated into the protein hemocyanin that serves as the oxygen-carrying mechanism in the blood (66).

In the present study, Cu concentrations were found to average 8 to 17 μg/l. This is far below the 1 mg/l standard set by USPHS.

Copper is generally more toxic to aquatic life in water of lower alkalinities. For the mayfly, Ephermerella subvaria, the 48-hour LC_{50} (42 mg/l alkalinity) was found to be 0.32 mg/l Cu^{++}. A 14-day LC_{50} of 32.0 mg/l Cu^{++} was found for the caddisfly Hydropsyche betteni at 42 mg/l alkalinity (46). The 96-hour LC_{50} for the fathead minnow, Pimephales promelas, was 75 μg/l (30 mg/l alkalinity) (69). Using the criterion set by EPA, 0.1 of the 96-hour LC_{50} for the fathead minnow determines the criterion to be 7.5 μg/l. Total Cu concentrations in Bull Run water were generally greater than this value and, thus, could affect this species of aquatic organism.

Mean metal concentrations and ranges found in Bull Run and other U.S. rivers are presented in Table 19. The Illinois River (37) receives domestic and industrial discharges from Chicago and other cities, while the Haw River(74) receives industrial and municipal discharges from Greensboro and other cities in North Carolina. Mean Ni, Pb and Cu concentrations in Bull Run were higher than those for the Illinois River, the Haw River, and the median values for other rivers reported by Bowen (75). Mean Zn concentrations were higher in Bull Run than the Haw River and the median Zn concentration reported by Bowen for the other rivers, but approximately the same for mean Zn concentrations in the Illinois River. Cr concentrations, however, in the Illinois River were three times greater than for Bull Run (perhaps reflecting the large quantities of industrial waste discharged into this river).

Table 20 presents average total metal loadings at Stations 1,

Table 19

Concentrations of Metals in Bull Run Water Compared with Those Reported for Other Rivers

	Concentration, μg/l							
	Bull Run		Illinois River[a]		Haw River[b]		Other Rivers[c]	
Metal	Mean	Range	Mean	Range	Mean	Range	Median	Range
Ni	34	2 - 106	2	1 - 6	--	--	10	0.2 - 20
Pb	10	2 - 16	2	1 - 18	4	--	5	0.6 - 120
Cd	1	1 - 1	0.6	0.1 - 2.0	1	--	8	--
Zn	30	1 - 55	31	1 - 610	7	--	10	0.2 - 1000
Cr	3	1 - 5	21	5 - 38	3	--	0.18	0.1 - 80
Cu	11	3 - 35	1	0.1 - 5	--	--	10	0.6 - 400

[a] (37)

[b] (26)

[c] (75)

Table 20

Average Metals Loadings at Station 1, 4, and 6 in Bull Run, July 30 to October 2, 1977

	Loadings, 10^4 lbs/day							
Station[a]	Fe	Mn	Ni	Pb	Cd	Zn	Cr	Cu
1	260	85	37	4	0.4	18	2	8
4	6,490	1,790	415	136	15	426	42	175
6	16,800	8,020	1,340	417	35	1,020	113	326

[a] see Figure 1 for location.

4, and 6. Fe loadings were the highest averaging 1.68 lb/day while Cd loadings were the lowest averaging 0.0035 lb/day. Loadings for the other metals were in the order: Mn > Ni > Zn > Pb > Cu > Cr. Metal loadings at Station 6 were higher than at Station 1 by 104 times for Pb, 94 times for Mn, 88 times for Cd, 65 times for Fe, 57 times for Zn and Cr, 41 times for Cu, and 36 times for Ni. No attempt will be made to extrapolate these average daily loadings to annual loadings since five sampling dates in the course of only three summer months are not representative of conditions found in a course of a total year.

Sediments. For the purpose of this study, a cold, acid-extraction technique (59) was used to remove only the weakly held, non-residual metals from the sediment. Hence, the metal concentrations in Bull Run sediments were difficult to compare with those reported in other studies where different analytical techniques were used. Furthermore, sediment characteristics, such as percent sand, silt, clay, organic carbon, and cation exchange capacity, can affect the retention of metals by sediments, thus making comparisons even more difficult.

Table 21 shows the characteristics of Bull Run sediments collected at each stream station. Sediments at Station 5, unlike those at the other sites, contained more fine sand than silt or clay. They also contained the least amounts of Fe, Mn, Ni, Zn, and Cr. Cd concentrations were the same for sediments at Station 1, 3, and 5. Cu in Station 5 sediments, however, was greater than at Stations 1 and 2. Furthermore, Pb in Station 5 sediments was greater than at Stations 1, 2, and 3.

Table 21

Characterization of Bull Run, Flat Branch, and Cub Run Sediments by Particle Size, Percent Organic Carbon, and Cation Exchange Capacity (CEC), Means and Variation

	Percent, Mean and Range				
Stream Station	Fine Sand (50-250 μ)	Silt (2-50 μ)	Clay (<2 μ)	Organic Carbon	CEC* meq/100 g
1	62	27	11	0.3	14
	58 - 66	23 - 31	10 - 12	0.2 - 0.4	
2	53	35	12	0.2	15
	41 - 60	26 - 48	8 - 16	0.1 - 0.3	
3	62	29	9	0.3	11
	44 - 71	21 - 39	5 - 11	0.2 - 0.4	
4	55	36	9	0.5	14
	52 - 58	28 - 40	5 - 14	0.3 - 0.6	
5	86	9	5	0.2	7
	80 - 89	6 - 15	3 - 6	0.1 - 0.3	
6	62	27	11	0.6	11
	47 - 74	18 - 42	8 - 13	0.5 - 0.9	
Flat Branch	--	--	--	--	18
Cub Run	--	--	--	--	8

*Summation of Exchangeable Cations (Ca, Mg, K, H).

Oliver (42) noted that particle size and surface area strongly influenced the extractable metal content of sediments. For instance, he found that Cu and Pb concentrations were 25 and 33 ppm within the silt-size fraction of one sample but only 5 and 9 ppm within the sand-size fraction. In the present study, however, Cu and Pb concentrations found in Station 5 sediment were, respectively, 1.5 and 1.9 times those in Station 1 sediment, even though sediment at Station 1 contained three times more silt than at Station 5. This anomaly indicates that Cu and Pb were present in much larger quantities at Station 5 than at Station 1.

The cation exchange capacity (CEC) for the Bull Run, Flat Branch, and Cub Run sediments are also found in Table 21. The CEC is a measure of a clay's (soil's or sediment's) ability to adsorb positive ions (cations). The CEC is expressed in terms of milliequivalents per 100 grams. Thus, if a soil has a CEC of 1 meq/100 g, it is capable of adsorbing and holding 1 mg of H^+, or its equivalent, for every 100 grams of dry substance (76). Station 5 sediments having a CEC of 7 meq/100 g, for example, have the capacity to retain 0.72 g Pb^{++} per 100 g sediment. Station 1 sediments, therefore, have the capacity to retain twice as much, or 1.44 g Pb^{++} per 100 g sediment. Based upon CEC data, Station 5 sediments have only one half the ability to adsorb Pb than do Station 1 sediments, but have an extractable Pb content of nearly twice that of Station 1 sediments. Again, this seems to indicate that more Pb was present downstream and was retained by downstream sediments.

The control mechanism responsible for sediments retaining metals can not be precisely defined using data obtained from this study. However, the relatively weak extraction procedure used in this study removed only those non-residual metals present as 1) exchangeable metals; 2) those present as carbonates, sulfides, and organic complexes; and 3) as the oxides and hydroxides of Mn and Fe (59) Retention mechanisms based upon these phases have been reported by many (39, 40, 43, 44). Jenne (38) however, proposed that the principal mechanism for retaining metals is the formation of hydrous oxide films of Mn and Fe, and that the other reported mechanisms play a significant but indirect role. Gibbs (29, 30) and Krauskopf (77) also have presented data in support of this proposition.

Hydrous metal oxides of Mn and Fe may form when ground water containing reduced Mn(II) and Fe(II) mixes with well oxygenated stream water. The reduced Mn(II) and Fe(II) oxidize to form fresh metal oxides which act as sinks for other metals in solution (78). Hem (79) has found it possible to explain this scavenging effect by means of oxidation-reduction equilibria at the $Fe(OH)_3$ surface.

If indeed, hydrous Mn and Fe oxide films play the major role in retaining metals on sediment particles, varying physio-chemical conditions could very well destroy the oxide films and release the metals into the water. Such a possibility becomes very real if these metal-laden sediments are carried into a lake or reservoir (80). Reducing conditions that develop in the hypolimnion because of summer stratification could destroy the oxide films and release the metals

Table 22

Heavy Metals Concentrations in Detritus Taken from Bull Run, and the Green River, Greenfield, Massachusetts

	Metal Concentrations in Detritus, μg/g			
	Bull Run		Green River[a]	
Metal	Station 1	Station 4	Station 1	Station 8
Fe	9,520	12,100	1,520	2,820
Mn	4,400	3,730	--	--
Ni	14	18	18	29
Pb	16	36	80	43
Cd	0.7	1.1	Not Detected	0.4
Zn	86	109	42	97
Cr	9	14	50	38
Cu	15	52	45	135

[a] (54)

into the water. Wetzel (81) claimed that Fe(II) ions diffuse readily from sediments when the redox potential decreases to +200 mv, and Mn(II) ions migrate from the sediment at somewhat higher redox potentials.

Detritus. Detritus has been described (81) as dead, particulate, organic matter inhabited by decomposer microorganisms. Large particulate organic matter, such as leaves, that enters a stream is a food source for many organisms (aquatic insects, bacteria, fungi) and becomes fine particulate organic matter to be ingested by other organisms. The detritus used in this study consisted of whole leaves that formed a mass consisting of the leaves and the associated living organisms. The organisms were individually picked out, and the leaves were dried, pulverized, and analyzed for metals.

To imply that these leaves were the major source of food for the caddisflies collected during this study, however, is not wholly valid. Kaushik and Hynes (82) found that some species of aquatic insects feed preferentially on different leaves (elm, maple, alder or oak, beech). Also, leaves colonized by microbial growth were preferred to those without any attached growths. Iverson (83) found that leaves present in a stream for one month or more were preferred by the caddisfly, Sericostoma personatum. Thus, leaves may travel a considerable distance downstream before being fed upon by aquatic organisms.

Comparisons of metals found in detritus for this study and the Greenfield, Massachusetts study (54) are presented in Table 22. The Green River drains the town of Greenfield, Massachusetts and receives wastes from combined sewers and a large storm channel. Above the town, the river drains sparsely populated areas consisting of mostly agricultural and forest lands. Cu, Cr, and Pb concentrations were much greater in detritus from the Green River than from Bull Run. Fe concentrations in detritus were greater in Bull Run than the Green River. Concentrations of the other metals in detritus were comparable for both studies. Metal concentrations in detritus were greater downstream in both studies for all metals except Pb, which was greater upstream in the Green River study. Apparently, the Green River receives more Pb from runoff than does Bull Run.

Caddisflies. Caddisflies used for this investigation were members of the family Hydropsychidae. Larvae of this family are known as "net spinners." The larva erects a net directly in front of a tubelike retreat that is concealed in a crevice or camouflaged by bits of wood, leaves, or other material. Small detrital particles, algae, and diatoms carried by the water current begin to accumulate in the net. The larva periodically cleans the net by ingesting anything edible (84).

Because of this feeding mechanism, Cummins (85) has classified larvae from this family as "collectors" or "filter feeders." Cummins has also classified this caddisfly as a hervibore-detritivore since its dominant food is living algal cells and decomposing organic matter. Generally, the insect feeds on particles smaller than 1000 μ in diameter. Thus, metal-containing detrital particles that have been reduced in size by other organisms are ingested by the caddisfly. Metals from

Table 23

Heavy Metals Concentration in Snails Taken from Bull Run, Missouri's New Lead Belt, and the Green River

	Metal Concentration in Snails, µg/g				
	Bull Run		New Lead Belt[a]		Green River[b]
Metal	Upstream	Downstream	Neals Creek	Strother Creek	Downstream
Fe	1,290	846	--	--	6,020
Mn	586	319	81	1,170	--
Ni	6	6	--	--	39
Pb	7	7	17	116	136
Cd	1	2	3	5	4
Zn	104	95	9	54	767
Cr	2	2	--	--	46
Cu	82	146	13	57	463

[a] (25)

[b] (54)

these detrital particles can then be accumulated by the caddisfly if there is no excretion mechanism whereby the organism can rid itself of the metal.

Caddisflies from the family Hydropsychidae (Hydropsyche) were also found at the upstream station in the Green River. Average metal concentrations (ppm) were reported to be: Fe, 2170; Cu, 31; Cr, 33; Ni, 44; Zn, 160; Pb, trace; and Cd, 5. Average metal concentrations (μg/g) in caddisflies from Bull Run at Station 1 were: Fe, 4,358; Cu, 21; Cr, 5; Ni, 19; Zn, 161; Pb, 9; and Cd, 2. Metal concentrations in caddisflies captured upstream in Bull Run appear to be comparable to those from the Green River.

Snails. Snails can feed by a variety of methods depending upon the species. Freshwater snails can either be herbivorous (feeing on algae or decaying organic matter) or carnivorous (benthic hunters). Many snails are sc rapers or grazers and feed on algae that cover rocks (86). Snails collected during this study (*Pleuocera sp.*) are scrapers and were found mainly among thick, benthic algae that covered the rocky stream substrate.

Metal concentrations in snails found in Bull Run are compared in Table 23 to metal concentrations in snails found in the Green River (54) and in two creeks of Missouri's "New Lead Belt" (25). Although both creeks are located within the area of Pb, Zn, Cu, and Ag ore deposits of Missouri's New Lead Belt, Neals Creek receives less mining and milling leachate from a tailings pond than does Strother Creek. Organisms were taken 4.0 mi downstream of a small tailings dam on Neals Creek and only

0.2 mi downstream of a rather large tailings dam on Strother Creek.

Snails taken from both stations (2 and 6) in Bull Run contained more Zn and Cu than those taken from both creeks in Missouri's New Lead Belt. Concentrations of Zn and Cu might be expected to be greater in snails taken from the New Lead Belt region because of the Zn and Cu ore deposits. As would be expected, concentrations of Pb in snails taken from Strother Creek were much greater than Pb concentrations in snails taken from Bull Run. However, all metal concentrations in snails taken from the downstream Green River Station were greater than in those taken either from Bull Run or the creeks of Missouri's Lead Belt.

Crayfish. Crayfish are often thought to be mainly scavengers. Some species, however, appear to eat living or recently killed animals and fresh vegetation in preference to decaying material. Larger specimens of Cambarus rubustus have been found to feed upon aquatic plants, while smaller ones fed upon aquatic insects (mayfly nymphs, chironomid and caddisfly larvae). Crayfish have often been known to kill and eat other crayfish which have recently molted and are still soft (87)

Crayfish in Bull Run did not concentrate Cd and Cr to any measurable extent. Crayfish concentrated Fe and Mn the least for all stream components. The metals Cu, Zn, and Pb were concentrated 36, 18, and 4 times that of Fe in crayfish. The very high concentration value for Cu may be due to a blood component, cyanoglobin, in the circulatory system of crayfish (57, 66).

Table 24 compares metal concentrations in crayfish taken from Bull Run, two creeks from Missouri's New Lead Belt, and two rivers from the Sudbury region in Ontario, Canada (57). The Wanapitei River drains the highly metal-contaminated areas near Ni-Cu smelters of the Sudbury region. The French River, however, drains uncontaminated areas east of Sudbury.

Crayfish taken from Bull Run at Station 4 contained lower concentrations of Mn, Ni, Pb, Cd, Zn, and Cu than crayfish taken from either Strother Creek or the Wanapitei River. Thus, it appears that metals originating from the Manassas urban area were concentrated by crayfish less than metals originating from the mining and smelting districts in Missouri and Ontario. In fact, all metals except Ni were less concentrated by upstream crayfish from Bull Run than control crayfish from Neals Creek and the French River. Therefore, it appears that crayfish concentrated metals greater in waters receiving larger metals input.

Stream Component Relationships

The highly significant linear correlations found for Pb concentrations among water, sediment, detritus, and caddisflies, and for Cu concentrations among water, sediment, detritus, caddisflies, and crayfish (Tables 14 and 15) suggest a relationship among the stream components for these two metals. It appears that crayfish, for example, could have accumulated Cu by eating caddisflies that had eaten copper contaminated detrital particles, etc. This oversimplification, however, ignores the

Table 24

Heavy Metals Concentration in Crayfish Taken from Bull Run, Missouri's New Lead Belt, and the Sudbury Region, Ontario

	Metal Concentration in Crayfish, μg/g					
	Bull Run		New Lead Belt[a]		Sudbury Region[b]	
Metal	Sta. 1	Sta. 4	Neals Creek	Strother Creek	French River	Wanapitei River
Mn	59	76	66	195	--	--
Ni	17	7	--	--	9	39
Pb	11	10	21	69	--	--
Cd	0	0	3	4	--	--
Zn	92	89	72	97	168	114
Cu	52	130	86	142	165	352

[a] (25)

[b] (57)

complexity of trophic relations and interactions of aquatic organisms within food webs that comprise a stream's ecosystem.

Odum (88) has pointed out that in a food web consisting of three major trophic levels (producer, primary consumer, secondary consumer), the caddisfly _Hydropsyche_ may occupy an intermediate position between the major trophic levels. Additionally, Cummins (85) has pointed out that based upon observed food habits, _Hydropsyche betteni_ has been reported in different systems to be predominantly a carnivore (89), a herbivore (90), and a herbivore-detritivore (91) by other investigators. Gut analysis of the caddisfly, _Glossosoma nigrior_, taken from two different streams revealed strikingly dissimilar food habits. For these reasons, Cummins has proposed that aquatic insects are polyphagous, or "generalists," and that food availability is the key to trophic relationships among aquatic insects. Classifying caddisflies from the family Hydropsychidae as strictly detritus feeders, for instance, ignores variations among species, habitat, and food availability.

Although mean Cu concentrations (found to be highly correlated among the stream components) were highest in the scavenger (and possibly predacious) crayfish, one must not conclude that biomagnification of copper has occurred and thus, threatens other organisms. The limited amount of data presented in this study and the complexity of relationships among organisms from a stream's ecosystem invalidate such a conclusion. Furthermore, other studies have found little evidence of biological magnification of Cu through the trophic levels(35, 57).

Hutchinson (57), for example, found crayfish to concentrate Cu by a factor of 39,111 from the surrounding water but omnivorous and carnivorous fish (bullhead and pickerel, respectively) were found to concentrate Cu by factors of only 149 and 156. For comparison, crayfish in this study concentrated Cu by a factor of 11,709.

This is not to imply, however, that any metal cannot be biologically concentrated through the trophic levels. Mercury has been found to be particularly troublesome in this respect. Armstrong and Hamilton (92) have concluded that once Hg is introduced into an ecosystem, it is "recycled by predation and scavenging, and can only be removed if organisms are bodily removed or if it can be excreted and perhaps sequestered by some nonliving component of the environment." It has also been found that Hg is excreted very slowly by fish and crayfish.

Armstrong and Hamilton (92) also found that Hg was concentrated greatest in the abdominal muscle of the crayfish, _Orconecter virilis_. Furthermore, a definite relationship existed between Hg concentration in the abdominal muscle of crayfish (both male and female) and body weight. Copper in crayfish from Bull Run, however, did not demonstrate any such relationship. Figure 29 shows a plot of Cu concentrations in crayfish as a function of carapace length. From this plot, it appears that Cu concentrations were not a function of crayfish age. Figure 30 shows that a slight possibility exists for Pb to decrease with crayfish size. Mettinen (93) presented data from another study (94) that suggested rainbow trout eliminated Cd from their bodies--the excretion

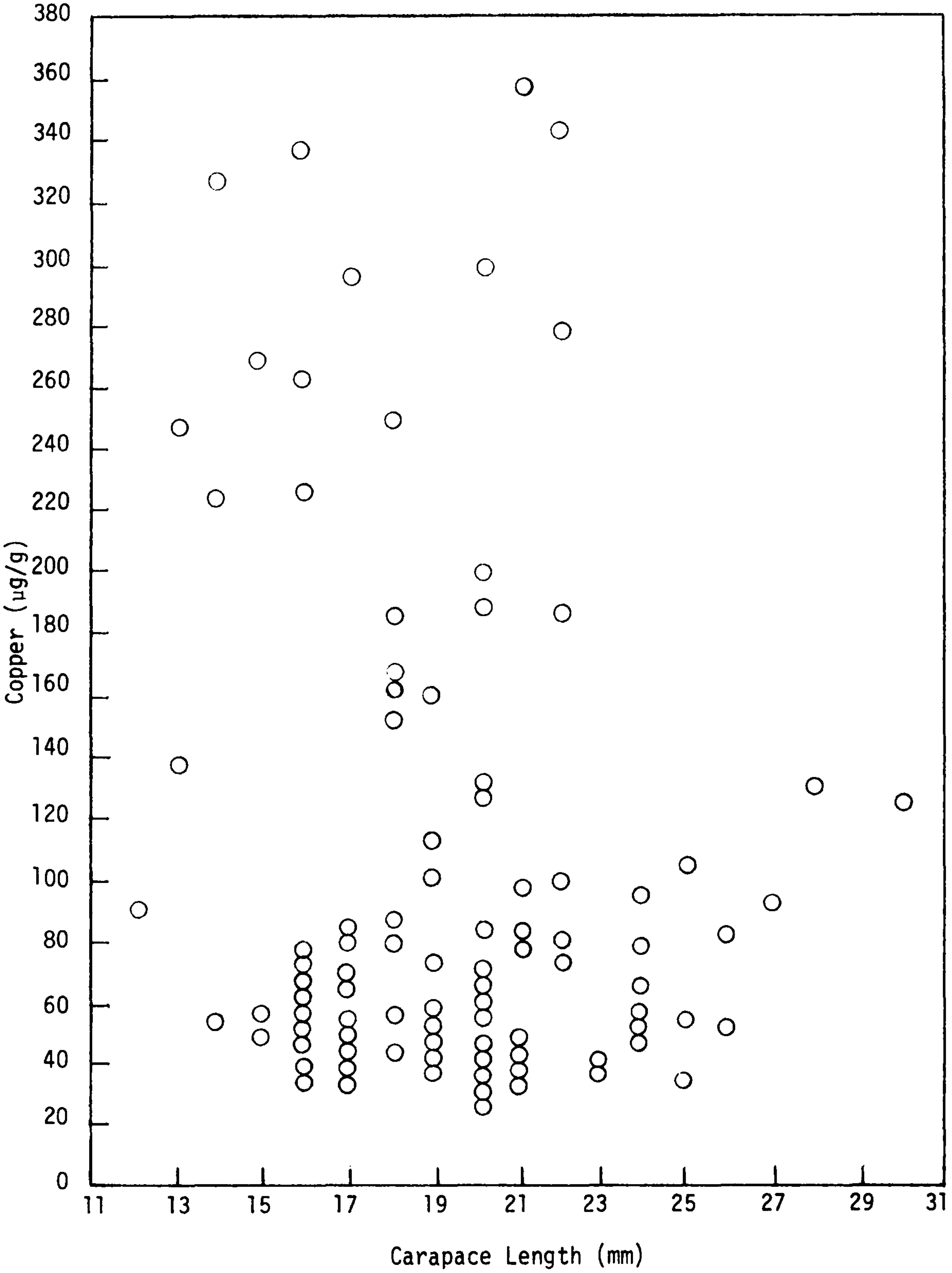


Figure 29. The relationship between size and concentration of copper in abdominal muscle for crayfish.

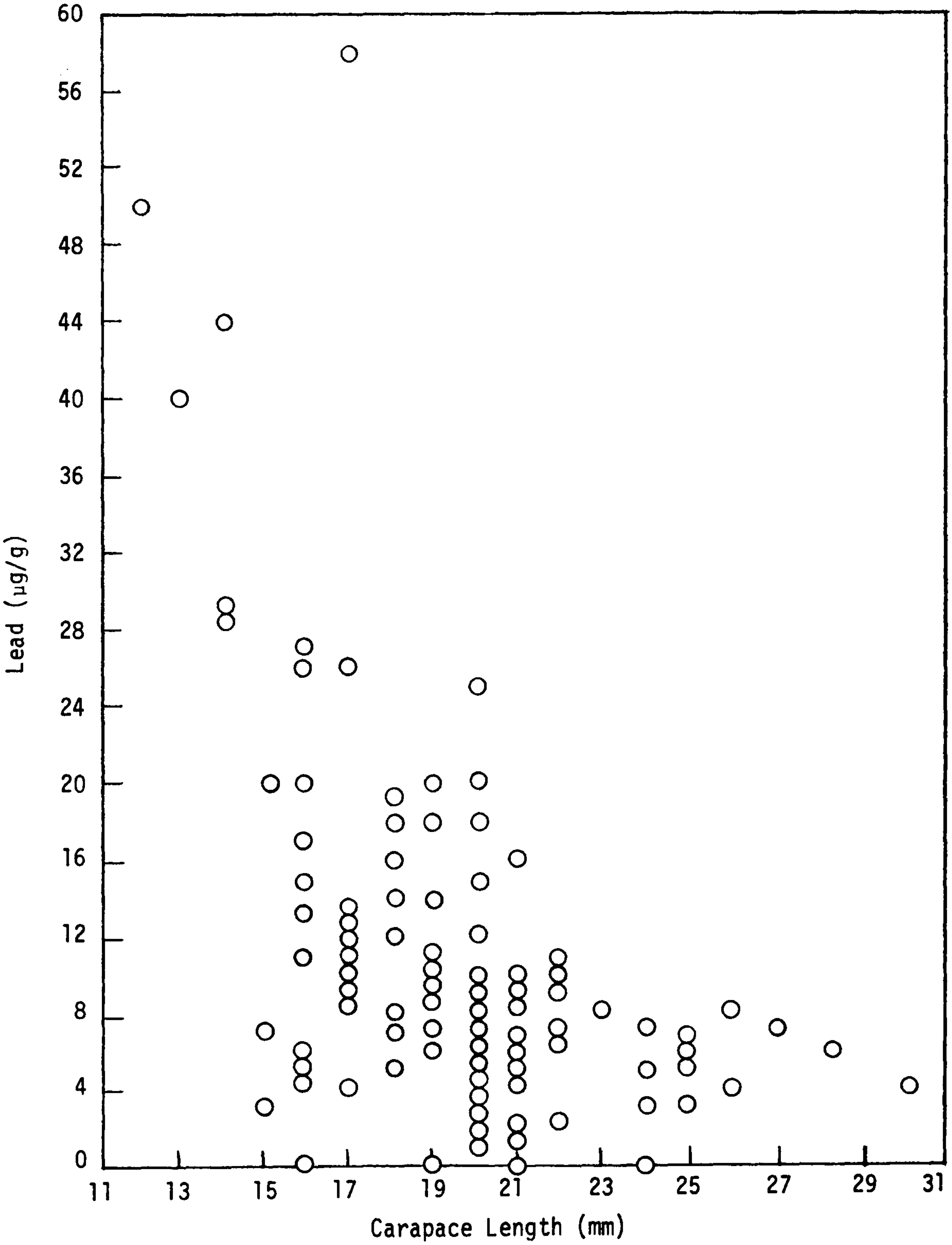


Figure 30. Relationship between size and concentrations of lead in abdominal muscle for crayfish.

rate following a power function--on a daily basis such that after 42 days only 1 percent of the administered dose was retained in the whole body. However, more data are needed to determine if crayfish were eliminating Pb from their bodies because only a few, large crayfish (greater than 21 mm) were analyzed. The vast majority were smaller.

VI. SUMMARY AND CONCLUSIONS

The purpose of this study was to determine the extent heavy metals contributed by urban runoff would be partitioned among the water, sediments, and resident biota in a stream that receives urban runoff and stormwater drainage. Sampling stations were established along Bull Run upstream and downstream of suspected stormwater inputs. Water, sediment, detritus, and benthos samples were collected on five separate occasions between July 30 and October 2, 1977. These samples were analyzed for concentrations of Fe, Mn, Ni, Pb, Cd, Zn, Cr, and Cu.

The significant conclusions derived from this study include the following:

1. Concentrations of all metals, except Mn, in water from Bull Run were less than the USPHS primary drinking water standard. Concentrations of Mn, however, should pose no threat to the public health. Additionally, concentrations of metals in water should not adversely affect aquatic life in Bull Run. Metal concentrations in water were found in the following order: Fe > Mn > Ni > Zn > Cu > Pb > Cr > Cd.

2. Concentration of metals in stream components found to be significantly greater downstream of the stormwater source (at Stations 4, 5, or 6) than at the upstream control, Station 1 were as follows: total Pb in water; dissolved Mn and Pb in water; Mn, Pb, Cd, Zn, Cu in sediment; Pb, Cr, and Cu in detritus; Pb and Cu in caddisflies; Cu in snails (comparing Station 6 to Station 2); and Cu in crayfish.

3. Only Cu and Pb could be shown to significantly accumulate in sediment, detritus, and caddisflies immediately below stormwater input (Station 4), and this concentration phenomenon persisted throughout the entire reach of the stream that was studied.

4. Concentrations of Pb in sediment at Station 5 (downstream of the stormwater input) were significantly greater than those at the upstream control, Station 1. Mean Cu concentrations in sediment were greater (but not significantly) at Station 5 than at Station 1. This was true even though the upstream sediment characteristics were such that metal retention was favored. All other metals were accumulated the least in sediments at Station 5.

5. Metals were concentrated by the various stream components over the concentration in water in the following order: Fe, detritus > sediment > caddisflies > snails > crayfish; Mn, detritus > caddisflies > sediment > snails > crayfish; Ni, detritus > caddisflies > crayfish > snails > sediment; Pb, detritus > caddisflies > sediment > crayfish > snails; Cd, caddisflies > snails > detritus > sediment; Zn, detritus > caddisflies > crayfish > snails > sediment; Cr, detritus > caddisflies> sediment > snails; Cu, snails > crayfish > caddisflies > detritus > sediment. Cu was the only metal that was concentrated greater by crayfish than by the other stream components. Crayfish did not concentrate Cd or Cr to any measureable extent.

6. Significant linear correlation coefficients among a majority of stream components were found for Pb and Cu. No other metal demonstrated as many significant correlations among stream components as did Pb and Cu.

7. It appears that urban runoff and stormwater drainage have contributed sufficient quantities of Pb and Cu into Bull Run such that these metals were accumulated greater in stream components below Manassas and Manassas Park than upstream of these areas.

VII. RECOMMENDATIONS

Further study is needed to determine whether fish in Bull Run are affected by (or concentrate) heavy metals (particularly Pb and Cu). Because significant concentrations of Pb and Cu were found in caddisflies below stormwater input to Bull Run, fish, that feed on caddisfly larvae, may begin to accumulate these metals. Although other studies (37, 57) have reported no evidence of biomagnification of heavy metals in fish, further work should be undertaken to investigate this possibility.

More work is also needed to determine by what mechanism sediment retains heavy metals. Depending upon the mechanism (formation of hydrous metal oxides, organo-metallic complexes, etc.), metals available to benthic organisms may be released into the water column more or less readily depending upon how the metals are retained onto the sediments.

Time variations of metal concentrations in stream components may also be studied. For instance, as urbanization increases in the Manassas area contributing more metals from urban runoff and stormwater drainage into Bull Run, will metals begin to accumulate in stream components greater than present levels? Also, downstream movement of metal-laden sediment and resuspension of sediment from scouring flows may be studied to determine possible long term effects that heavy metals in Bull Run may have upon the Occoquan Reservoir.

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APPENDICES

Table A1

Summary of Physical, Chemical, and Hydrological Stream Data for Bull Run, July 30, 1977

Parameter	Stream Station*					
	1	2	3	4	5	6
pH	7.2	7.0	6.5	6.5	6.8	--
Temperature, °C	29	27	27	24	26	--
Dissolved oxygen, mg/l	9.1	9.4	8.2	7.5	8.3	--
Total alkalinity, mg/l $CaCO_3$	74	78	71	67	82	--
Total hardness, mg/l $CaCO_3$	80	98	82	116	194	--
Total organic carbon, mg/l	15	8	14	25	--	--
Total suspended solids, mg/l	6	9	10	11	12	--
Volatile suspended solids, mg/l	1	1	2	1	1	--
Gage height, ft	1.44	--	--	1.24	--	--
Flow, cfs	0.03	--	--	5.0	--	--

*See Figure 1 in text.

Table A2

Summary of Physical, Chemical, and Hydrological Stream Data for Bull Run, August 11, 1977

Parameter	Stream Station*					
	1	2	3	4	5	6
pH	5.8	6.4	6.0	6.8	6.8	6.5
Temperature, °C	26	28	29	29	28	26
Dissolved oxygen, mg/l	7.1	7.2	6.4	6.7	7.0	4.8
Total alkalinity, mg/l $CaCO_3$	77	70	68	68	78	64
Total hardness, mg/l $CaCO_3$	76	82	86	96	130	117
Total organic carbon, mg/l	10	11	13	15	20	11
Total suspended solids, mg/l	8	10	6	12	6	6
Volatile suspended solids, mg/l	2	2	2	2	2	2
Gage height, ft	1.6	--	--	1.28	-	1.12
Flow, cfs	0.20	--	--	9.8	--	26

*See Figure 1 in text.

Table A3

Summary of Physical, Chemical, and Hydrological Stream Data for Bull Run, August 31, 1977

Parameter	Stream Station*					
	1	2	3	4	5	6
pH	5.5	6.3	6.3	6.3	6.3	6.3
Temperature, °C	24	25	26	26	27	25
Dissolved oxygen, mg/l	6.9	7.0	5.0	5.6	4.8	6.3
Total alkalinity, mg/l $CaCO_3$	61	47	49	70	104	72
Total hardness, mg/l $CaCO_3$	62	58	58	95	163	109
Total organic carbon, mg/l	14	14	10	10	12	9
Total suspended solids, mg/l	12	10	7	11	7	11
Volatile suspended solids, mg/	4	3	1	1	2	1
Gage height, ft	1.63	--	--	1.26	--	0.91
Flow, cfs	0.62	--	--	5.4	--	13.0

*See Figure 1 in text.

Table A4

Summary of Physical, Chemical, and Hydrological Stream Data for Bull Run, September 25, 1977

Parameter	Stream Station*					
	1	2	3	4	5	6
pH	7.1	7.2	6.3	5.8	6.0	6.1
Temperature, °C	20	21	21	21	22	21
Dissolved oxygen, mg/l	5.0	7.4	6.7	5.9	5.4	4.5
Total alkalinity, mg/l $CaCO_3$	57	67	63	72	129	86
Total hardness, mg/l $CaCO_3$	68	77	76	114	195	135
Total organic carbon, mg/l	12	9	13	12	15	11
Total suspended solids, mg/l	10	5	6	4	3	7
Volatile suspended solids, mg/l	3	2	2	3	2	3
Gage height, ft	1.55	--	--	1.30	--	0.90
Flow, cfs	0.11	--	--	6.3	--	12.3

*See Figure 1 in text.

Table A5

Summary of Physical, Chemical, and Hydrological Stream Data for Bull Run, October 2, 1977

Parameter	Stream Station*					
	1	2	3	4	5	6
pH	7.2	7.2	7.2	6.4	7.2	6.2
Temperature, °C	20	19	21	19	21	19
Dissolved oxygen, mg/l	5.5	7.6	7.8	4.7	4.8	3.8
Total alkalinity, mg/l $CaCO_3$	70	72	74	92	142	117
Total hardness, mg/l $CaCO_3$	78	81	77	150	212	184
Total organic carbon, mg/l	16	16	14	22	21	81
Total suspended solids, mg/l	4	2	3	7	3	5
Volatile suspended solids, mg/l	2	1	2	3	2	2
Gage height, ft	1.55	--	--	1.30	--	0.85
Flow, cfs	0.11	--	--	6.3	-	10.0

*See Figure 1 in text.

Table B1

Total and Dissolved Metal Concentrations in Stream Water, Bull Run, July 30-October 2, 1977

Date	Station	Metal Concentration, µg/l															
		Fe		Mn		Ni		Pb		Cd		Zn		Cr		Cu	
		Dis	Tot	Dis	Tot	Dis	Tot	Dis	Tot	Dis	Tot	Dis	Tot	Dis	Tot	Dis	Tot
7/30/77	1	455	608	58	180	8	16	6	7	1	1	20	17	1	3	11	5
	2	101	641	34	192	5	20	6	6	1	1	13	13	0	3	4	4
	3	136	543	64	119	4	26	6	7	1	1	8	16	0	3	4	5
	4	177	508	176	189	19	18	11	11	1	1	6	8	2	4	30	35
	5	75	348	151	162	8	9	16	15	1	1	9	1	2	3	13	12
	6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8/11/77	1	106	420	34	181	0	106	7	12	1	1	13	55	1	3	1	10
	2	91	327	46	176	0	82	3	9	1	1	10	52	2	3	1	10
	3	79	271	48	91	0	49	4	8	1	1	8	24	1	4	1	6
	4	180	544	120	145	1	64	7	12	1	1	8	41	1	4	6	15
	5	103	312	140	154	14	27	10	12	1	1	4	20	1	3	16	9
	6	130	482	191	219	0	60	6	13	1	1	6	31	2	4	3	9
8/31/77	1	108	560	37	193	0	95	4	9	1	1	36	34	1	3	1	22
	2	333	810	57	235	0	85	9	14	1	1	20	27	1	5	2	17
	3	383	773	79	100	0	79	4	11	1	1	10	48	1	3	1	17
	4	247	627	141	165	0	54	6	9	1	1	17	38	1	3	4	19
	5	208	550	218	230	0	41	16	12	1	1	12	35	2	3	5	16
	6	224	693	325	374	0	48	9	18	1	1	10	37	1	3	3	18

Table B1 (Continued)

Date	Station	Metal Concentration, µg/l															
		Fe		Mn		Ni		Pb		Cd		Zn		Cr		Cu	
		Dis	Tot	Dis	Tot	Dis	Tot	Dis	Tot	Dis	Tot	Dis	Tot	Dis	Tot	Dis	Tot
9/25/77	1	154	900	157	171	2	12	3	4	1	1	31	36	2	3	3	6
	2	88	273	28	67	2	8	4	6	1	1	17	37	2	1	2	3
	3	120	329	34	48	2	5	4	5	1	1	21	32	2	2	2	4
	4	92	226	101	68	4	2	10	9	1	1	30	49	3	1	5	6
	5	91	213	134	137	6	15	13	16	1	1	14	22	3	2	5	9
	6	75	396	101	120	5	4	11	13	1	1	18	23	2	3	3	5
10/2/77	1	76	263	48	90	3	9	3	3	1	1	22	31	1	1	3	11
	2	60	174	26	46	3	10	5	5	1	1	22	31	1	1	2	8
	3	96	270	38	53	4	2	4	2	1	1	17	22	1	1	1	7
	4	139	277	122	132	5	8	9	10	1	1	16	25	1	2	5	8
	5	103	202	162	165	8	18	15	15	1	1	17	40	1	3	5	13
	6	83	345	205	222	7	14	12	14	1	1	15	25	2	2	4	5

Tot = Total Metals

Dis = Dissolved Metals

Table B2

Extractable Metals From Sediments

		Extractable Metals, µg/g*							
Date	Station	Fe	Mn	Ni	Pb	Cd	Zn	Cr	Cu
7/31/77	1	5730	664	4.2	8.5	0.1	11.1	2.7	4.2
	2	7500	746	4.7	9.3	0.2	8.2	3.6	4.7
	3	4140	394	2.0	12.1	0.2	10.3	2.7	8.6
	4	5550	765	2.2	25.8	0.4	21.1	3.1	24.0
	5	3060	457	0.9	17.6	0.2	10.8	2.1	7.4
	6	--	--	--	--	--	--	--	--
8/12/77	1	6120	642	5.3	8.7	0.2	13.0	2.7	4.2
	2	8120	726	6.4	7.8	0.2	14.0	3.8	5.2
	3	4484	345	3.5	14.3	0.2	13.5	3.0	9.6
	4	5130	548	2.5	21.6	0.2	16.7	2.6	17.1
	5	2380	325	1.1	15.0	0.2	9.7	1.9	6.6
	6	3390	269	2.8	14.9	0.2	14.4	2.8	7.2
9/1/77	1	4190	531	5.2	7.2	0.1	12.2	2.4	3.8
	2	5470	664	4.4	8.4	0.2	9.1	3.2	3.9
	3	3260	327	2.6	10.1	0.1	10.0	2.4	5.7
	4	3500	536	3.3	14.9	0.2	11.8	2.4	1.1
	5	1810	216	2.0	13.9	0.1	8.8	1.8	4.6
	6	2690	300	2.7	14.7	0.2	15.4	2.5	7.6
9/24/77	1	4590	561	4.7	8.1	0.1	9.9	2.2	3.9
	2	5700	655	5.2	7.1	0.1	9.9	2.9	4.1
	3	3370	261	2.5	10.9	0.1	10.4	2.3	5.7
	4	4960	1050	3.5	20.5	0.2	22.3	2.1	9.0
	5	2100	284	2.3	17.2	0.1	9.7	1.7	5.8
	6	3260	310	3.1	14.5	0.1	17.7	2.5	8.9
10/1/77	1	5000	632	4.8	8.5	0.1	11.8	2.6	4.2
	2	5740	702	3.6	8.3	0.1	10.8	3.0	4.1
	3	3690	321	2.0	12.5	0.1	11.0	2.6	6.7
	4	4980	1170	3.2	25.0	0.3	20.0	2.7	11.4
	5	1940	263	1.2	14.1	0.1	9.7	1.6	6.0
	6	4190	462	3.4	20.3	0.3	20.5	3.2	11.9

*Extraction with 0.5 N HCl for 12 hrs. at room temperature.

Table B3

Metal Concentrations in Detritus*

		Metal Concentrations, µg/g							
Date	Station	Fe	Mn	Ni	Pb	Cd	Zn	Cr	Cu
7/31/77	1	10600	6990	16.3	20.3	0.6	88.6	8.9	16.3
	2	7180	2940	13.8	37.0	0.3	82.9	7.7	16.4
	3	6360	1310	17.0	25.9	1.1	78.2	7.6	33.6
	4	6370	1610	15.5	30.1	1.4	134	9.1	77.6
	5	8330	4920	16.2	36.1	0.5	123	10.4	59.7
	6	--	--	--	--	--	--	--	--
8/12/77	1	10600	3960	13.7	16.8	0.3	108	12.1	12.4
	2	11900	4340	18.3	23.0	1.1	83.4	11.0	14.1
	3	4350	945	14.1	24.8	1.3	53.3	8.4	23.0
	4	15200	3600	20.6	43.3	0.9	138	19.9	58.5
	5	15700	3690	20.5	40.0	0.2	161	16.0	49.5
	6	10000	2580	18.7	20.3	1.8	162	11.0	37.9
9/1/77	1	11100	4210	15.8	16.1	0.8	49.2	9.0	15.7
	2	9630	2310	14.9	18.4	0.8	46.1	8.9	13.4
	3	4240	1840	9.8	19.7	0.9	87.6	5.0	14.6
	4	14400	5420	19.1	46.4	1.2	73.4	12.6	61.9
	5	10630	2680	14.4	30.2	0.8	72.5	10.4	33.9
	6	8630	5150	14.1	21.5	0.9	70.3	11.3	20.4
9/24/77	1	6750	3330	12.3	12.8	0.9	117	4.5	16.5
	2	7660	3120	19.6	15.9	1.3	122	5.3	14.3
	3	7660	1500	12.8	22.6	0.8	108	9.1	22.6
	4	13000	4100	17.9	32.5	1.1	122	16.2	33.2
	5	6900	3210	11.5	25.4	0.7	96.1	8.7	21.9
	6	7010	4190	13.1	18.9	0.8	117	7.4	18.5
10/1/77	1	8570	3720	10.4	17.1	0.9	66.2	8.7	11.7
	2	8640	3720	11.9	23.9	0.8	124	7.7	13.9
	3	2400	813	7.9	16.4	0.7	64.0	5.7	11.5
	4	11300	3900	14.9	28.4	0.9	75.2	13.2	27.4
	5	9520	5300	13.6	23.2	0.7	71.4	13.3	31.5
	6	8260	5140	15.4	23.7	1.1	82.6	14.4	19.8

*Detritus: Test whole leaves and associated material adhering to the leaves.

Table B4

Metal Concentrations in Caddisflies

		Metal Concentrations, µg/g							
Date	Station	Fe	Mn	Ni	Pb	Cd	Zn	Cr	Cu
7/31/77	1	4600	2280	20.0	8.4	1.4	200	6.0	23.3
	2	3650	2140	6.1	12.6	1.0	145	3.5	25.7
	4	4630	1540	11.4	30.9	1.7	153	6.9	114
	6	--	--	--	--	--	--	--	--
8/12/77	1	2960	1920	22.7	8.7	1.2	144	3.5	25.0
	2	3230	2170	6.1	12.6	1.0	145	3.5	25.7
	4	3380	1130	14.3	22.5	2.3	156	4.5	65.4
	6	2300	1500	17.0	10.0	1.0	124	2.5	33.5
9/1/77	1	2580	1920	11.9	4.6	1.3	144	3.3	21.9
	2	--	--	--	--	--	--	--	--
	4	3250	890	8.9	28.1	3.7	168	3.7	47.4
	6	3140	1730	17.3	10.5	1.2	152	3.1	30.1
9/24/77	1	5590	2750	22.0	11.9	1.8	153	6.4	17.0
	2	--	--	--	--	--	--	--	--
	4	3200	1680	6.9	18.3	1.5	173	6.1	35.9
	6	6010	3230	20.6	17.9	1.3	147	6.3	30.0
10/1/77	1	6060	2810	19.1	12.4	1.7	167	5.1	17.9
	2	3950	1740	7.7	12.3	1.0	163	3.6	20.0
	4	3570	1990	17.3	21.4	1.0	172	4.1	41.8
	6	6720	3330	16.6	20.1	3.4	153	6.9	30.4

Table B5

Metal Concentrations in Snails

Date	Station	Fe	Mn	Ni	Pb	Cd	Zn	Cr	Cu
		Metal Concentrations, µg/g							
7/31/77	2	1410	726	5.6	8.4	0.9	92.3	2.9	75.7
	6	--	--	--	--	--	--	--	--
8/12/77	2	1080	840	5.4	5.9	1.4	109	1.9	56.3
	6	662	325	5.6	7.0	1.2	121	1.5	129
9/1/77	2	740	400	4.4	5.5	1.2	77.4	1.4	70.0
	6	819	380	4.8	7.4	2.1	91.8	1.4	126
9/24/77	2	1810	495	6.8	10.1	1.8	97.5	2.8	94.0
	6	1300	378	6.9	7.6	1.9	105	2.6	169
10/1/77	2	1390	469	6.3	7.2	1.0	97.5	2.4	116
	6	601	191	5.1	6.0	1.6	97.3	1.2	158

Table B6

Metal Concentrations in Crayfish*

		Average Metal Concentration, µg/g							
Date	Station	Fe	Mn	Ni	Pb	Cd	Zn	Cr	Cu
7/31/77	1	548	64.5	45.2	25.8	0.0	119	0.0	51.6
	2	220	150	20.8	28.6	0.0	95.2	0.0	54.0
	3	224	101	48.5	35.3	0.0	93.4	0.0	176
	4	212	115	10.1	21.0	0.0	96.3	0.0	265
	5	148	112	31.1	21.2	0.0	79.2	0.0	180
	6	--	--	--	--	--	--	--	--
8/12/77	1	110	91.0	17.9	11.7	0.0	87.7	0.0	58.6
	2	95	95.3	16.6	11.9	0.0	106	0.0	56.5
	3	114	50.9	14.2	9.7	0.0	81.9	0.0	202
	4	135	51.2	7.7	11.6	0.0	85.5	0.0	165
	5	200	144	13.4	11.5	0.0	81.9	0.0	300
	6	76.5	63.0	6.0	7.1	0.0	93.6	0.0	96.8
9/1/77	1	119	85.9	4.9	8.2	0.0	92.1	0.0	46.3
	2	111	77.9	4.3	8.5	0.0	83.7	0.0	60.0
	3	135	59.6	5.6	9.9	0.0	80.3	0.0	83.2
	4	176	73.6	8.1	6.9	0.0	89.0	0.0	113
	5	43.0	31.7	4.9	5.6	0.0	123	0.0	135
	6	68.5	67.5	6.3	6.2	0.0	84.6	0.0	89.7
9/24/77	1	60.5	19.9	6.0	1.8	0.0	86.0	0.0	49.5
	2	122	42.6	0.0	6.5	0.0	73.3	0.0	45.0
	3	106	42.8	77.3	6.3	0.0	75.2	0.0	59.1
	4	131	71.4	1.5	3.3	0.0	89.9	0.0	45.9
	5	72.4	36.2	1.9	1.9	0.0	99.0	0.0	85.7
	6	98.4	38.6	4.7	6.9	0.0	80.5	0.0	52.6
10/1/77	1	85.9	31.3	11.6	9.7	0.0	73.6	0.0	51.7
	2	42.7	41.6	3.3	1.7	0.0	71.3	0.0	62.1
	3	91.6	64.0	7.6	3.4	0.0	85.2	0.0	69.8
	4	129	66.6	7.0	7.6	0.0	86.1	0.0	62.1
	5	108	63.9	2.8	11.1	0.0	72.2	0.0	52.8
	6	94.5	371	1.2	4.3	0.0	127	0.0	132

*The abdominal muscle was used for the analysis.

Table C1

Characterization of Sediments by Percent Sand, Silt, Clay, and Organic Carbon for the Six Stream Stations and Five Sampling Dates

		Percent			
Date	Station	Fine Sand (50-250 μ)	Silt (2-50 μ)	Clay (< 2μ)	Organic Carbon
7/31/77	1	58	31	11	0.4
	2	41	48	11	0.3
	3	50	39	11	0.3
	4	55	37	8	0.5
	5	80	15	5	0.3
	6	--	--	--	--
8/12/77	1	60	29	11	0.3
	2	44	40	16	0.2
	3	57	35	8	0.4
	4	55	37	8	0.5
	5	88	9	3	0.2
	6	74	18	8	0.5
9/1/77	1	63	25	12	0.2
	2	60	28	12	0.1
	3	63	26	11	0.2
	4	58	28	14	0.3
	5	87	7	6	0.1
	6	60	27	13	0.5
9/24/77	1	66	23	11	0.3
	2	60	32	8	0.2
	3	71	24	5	0.2
	4	52	37	11	0.5
	5	89	6	5	0.1
	6	68	21	11	0.6
10/1/77	1	63	27	10	0.3
	2	58	26	16	0.2
	3	68	21	11	0.3
	4	55	40	5	0.6
	5	88	7	5	0.2
	6	47	42	11	0.9

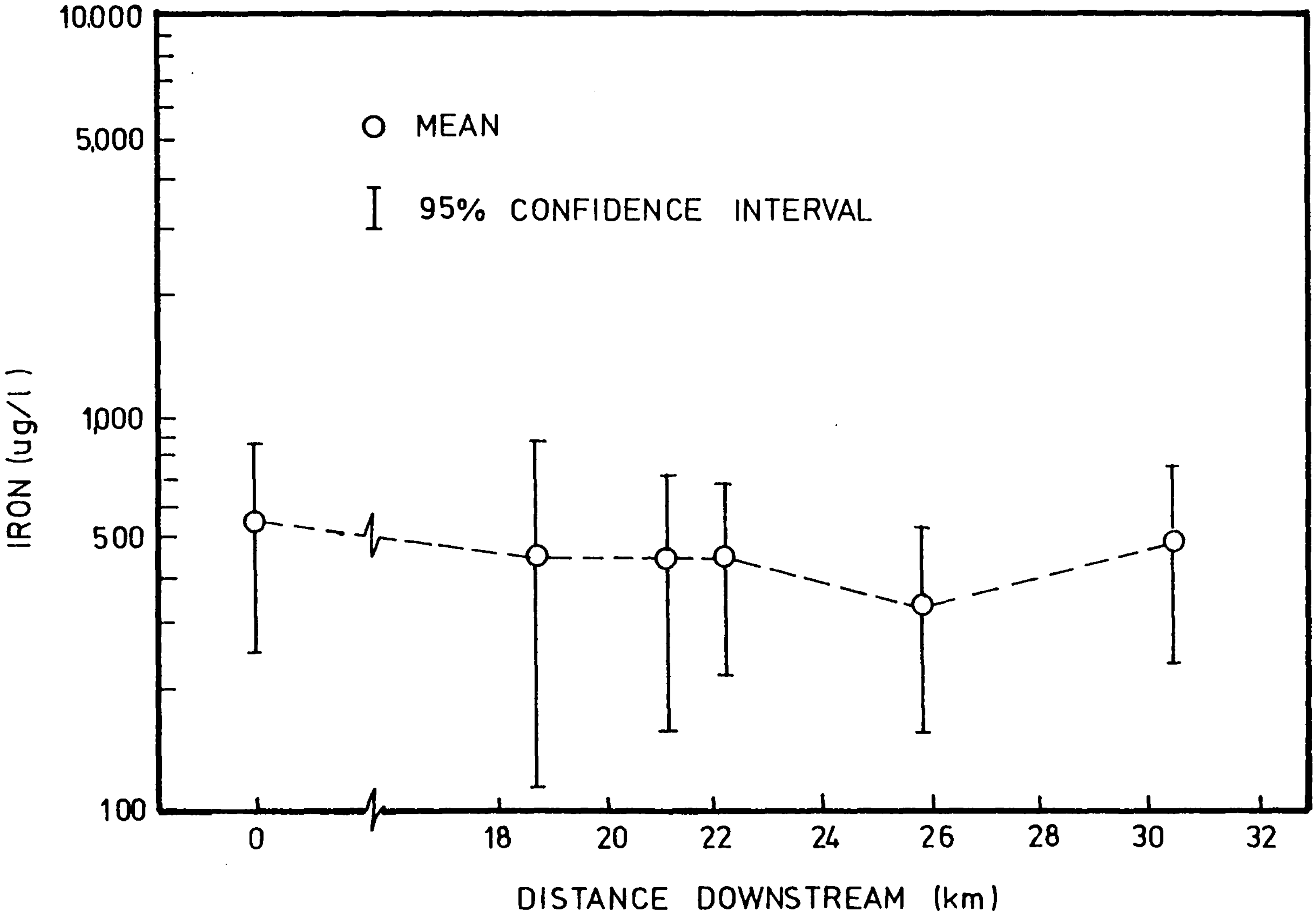

Figure D1. Total iron concentrations in water at all six Bull Run stream stations.

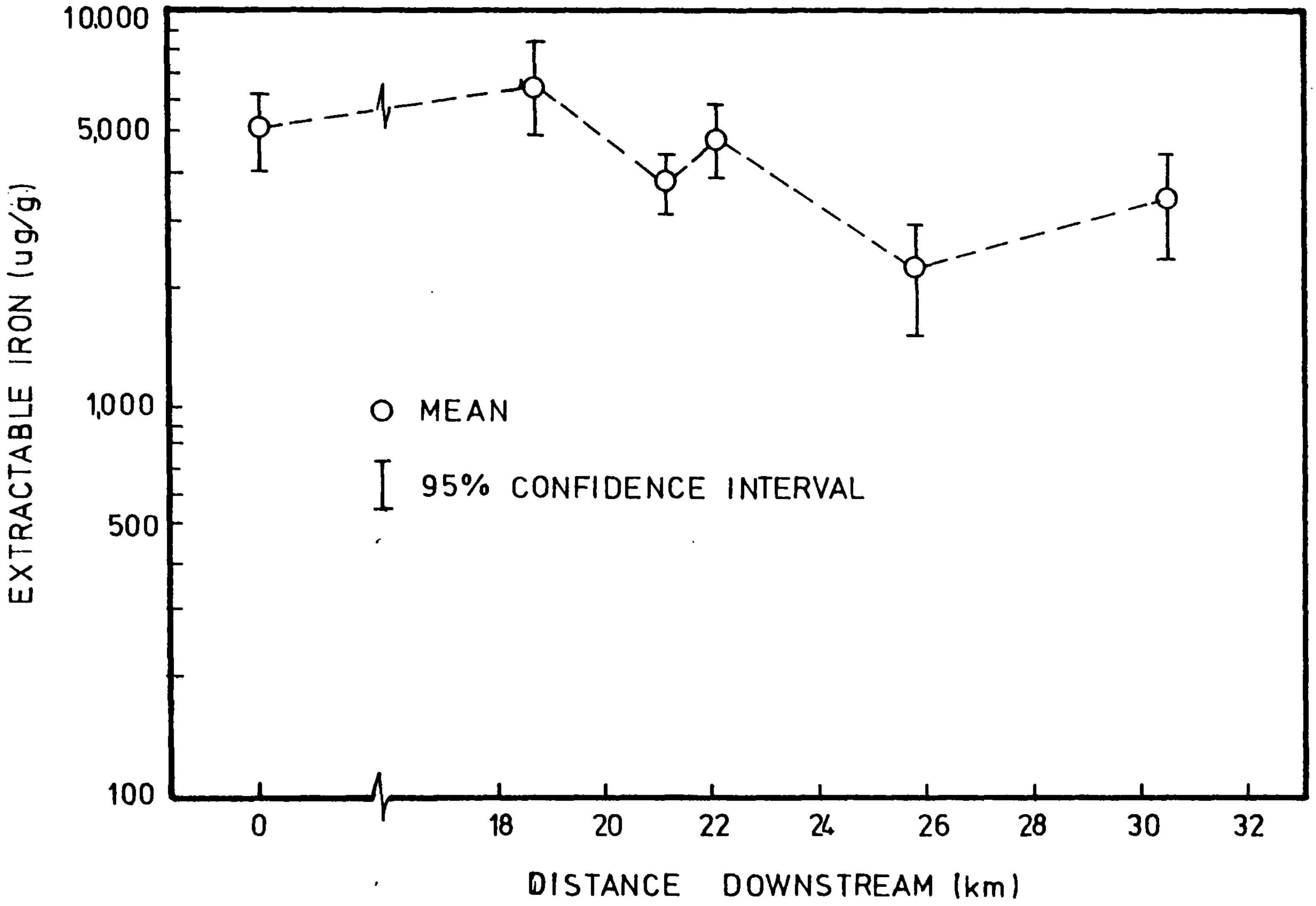

Figure D2. Extractable iron in sediments from all six Bull Run stream stations.

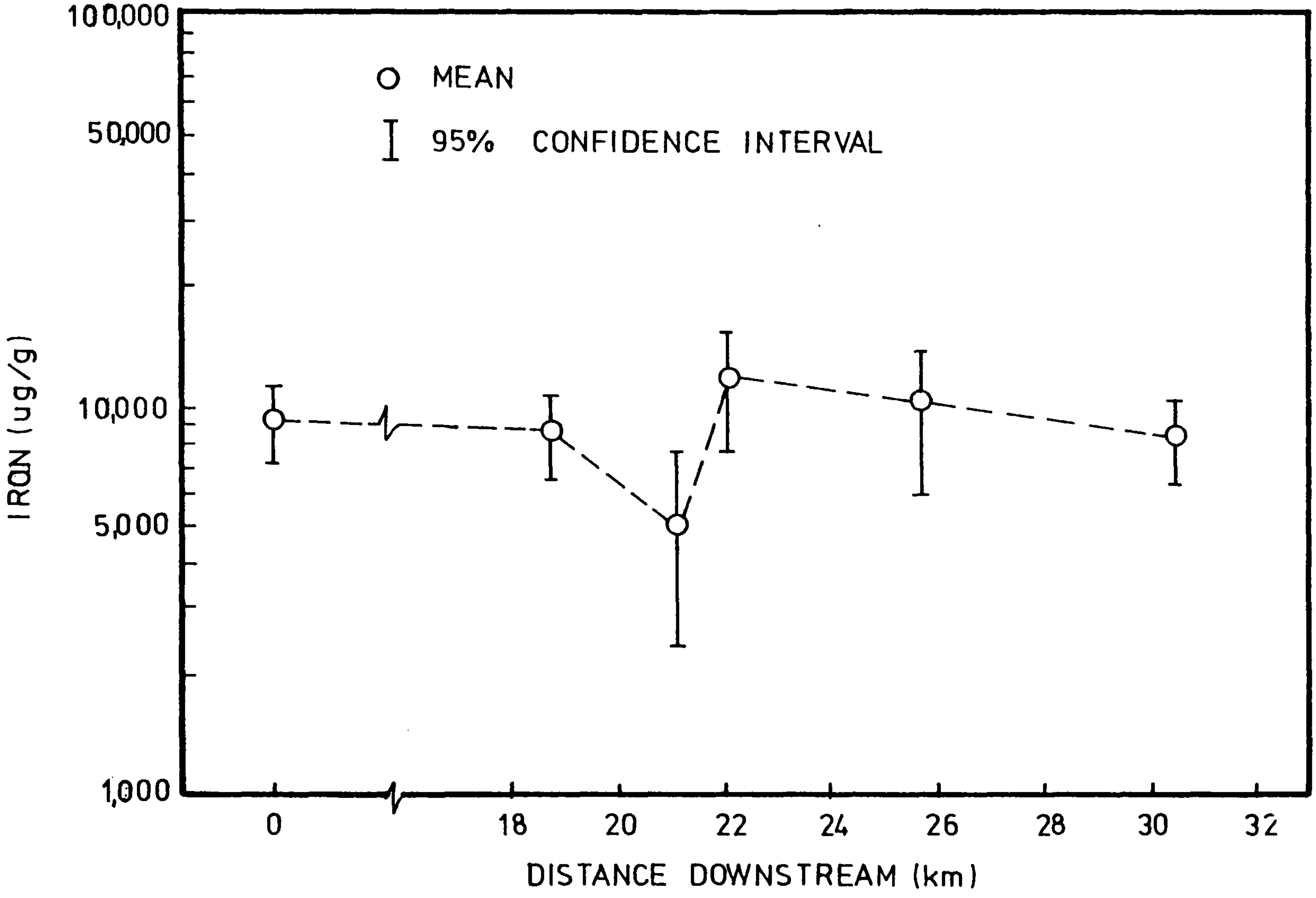

Figure D3. Iron concentrations in detritus from all six Bull Run stream stations.

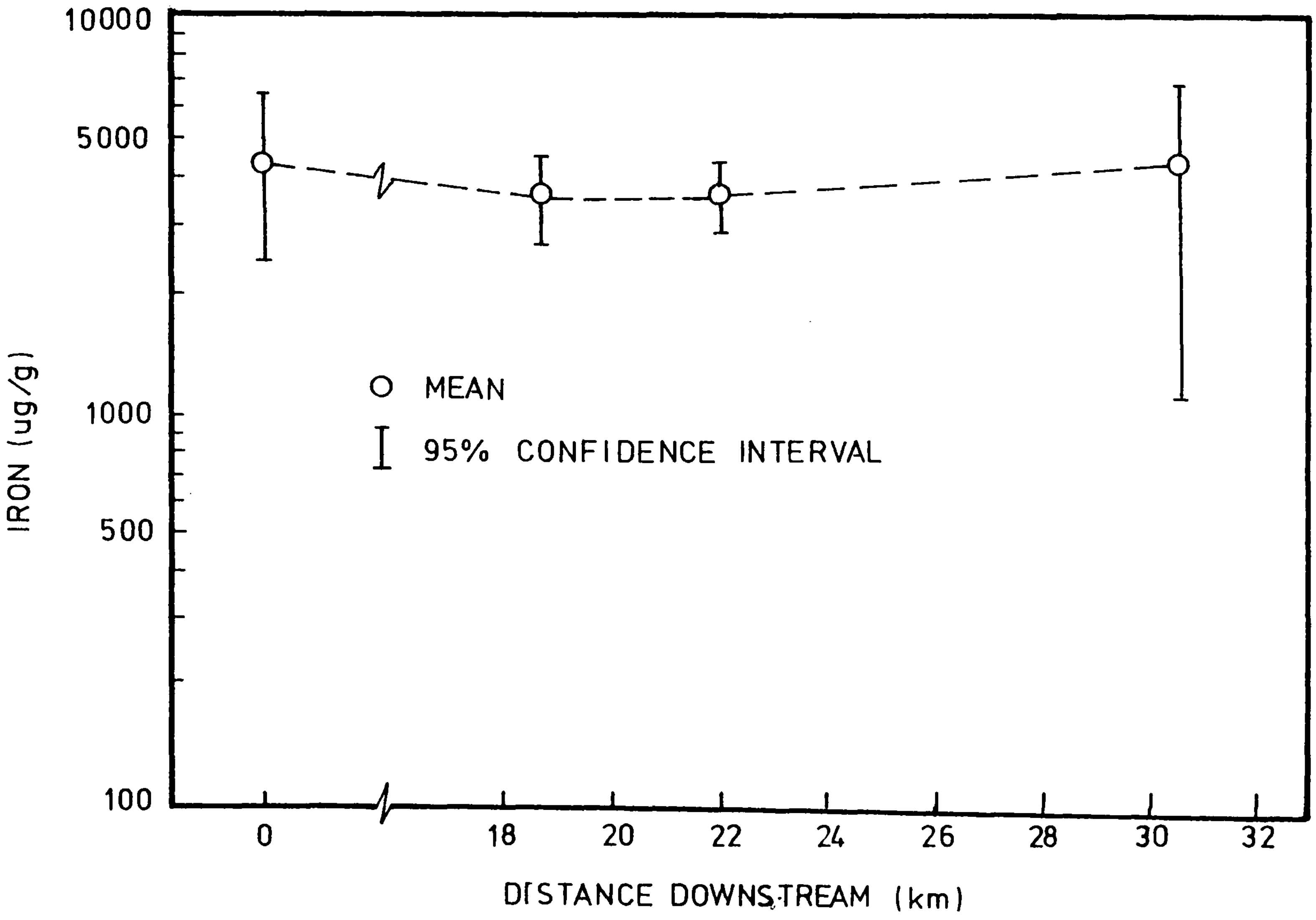

Figure D4. Iron concentrations in caddisflies from Bull Run Stations 1, 2, 4, and 6.

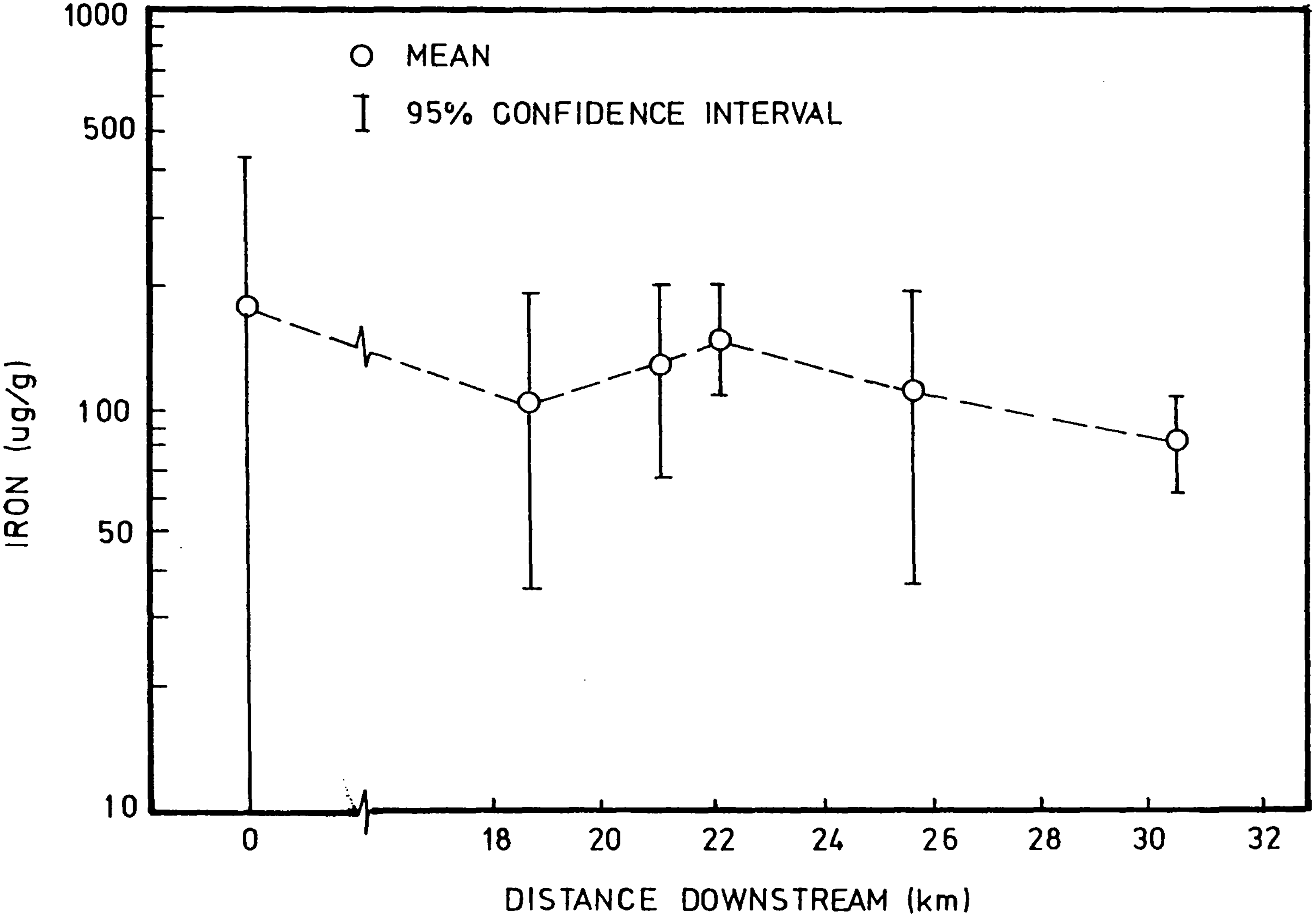

Figure D5. Iron concentrations in crayfish from all six Bull Run stream stations.

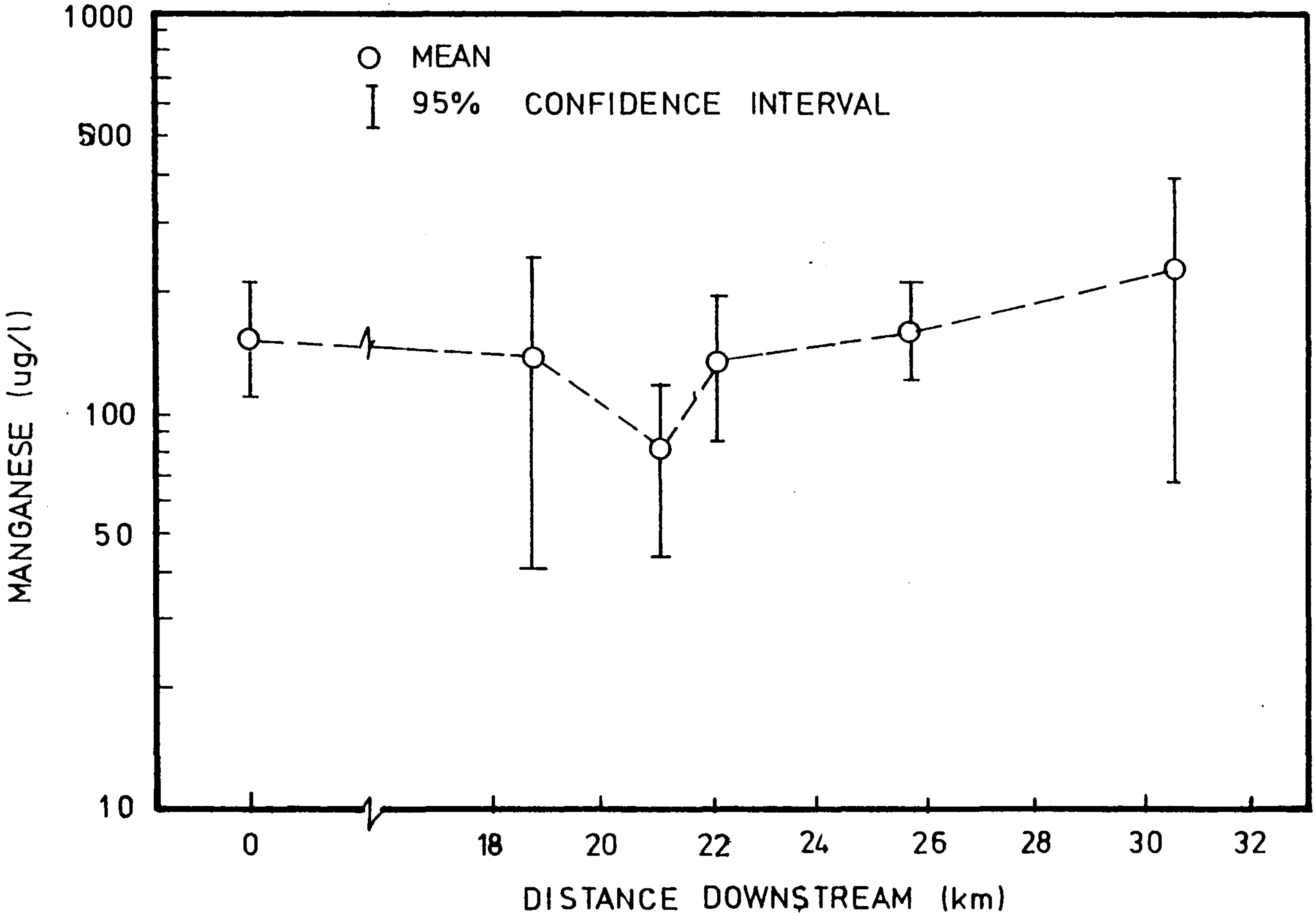

Figure D6. Total manganese concentrations in water at all six Bull Run stream stations.

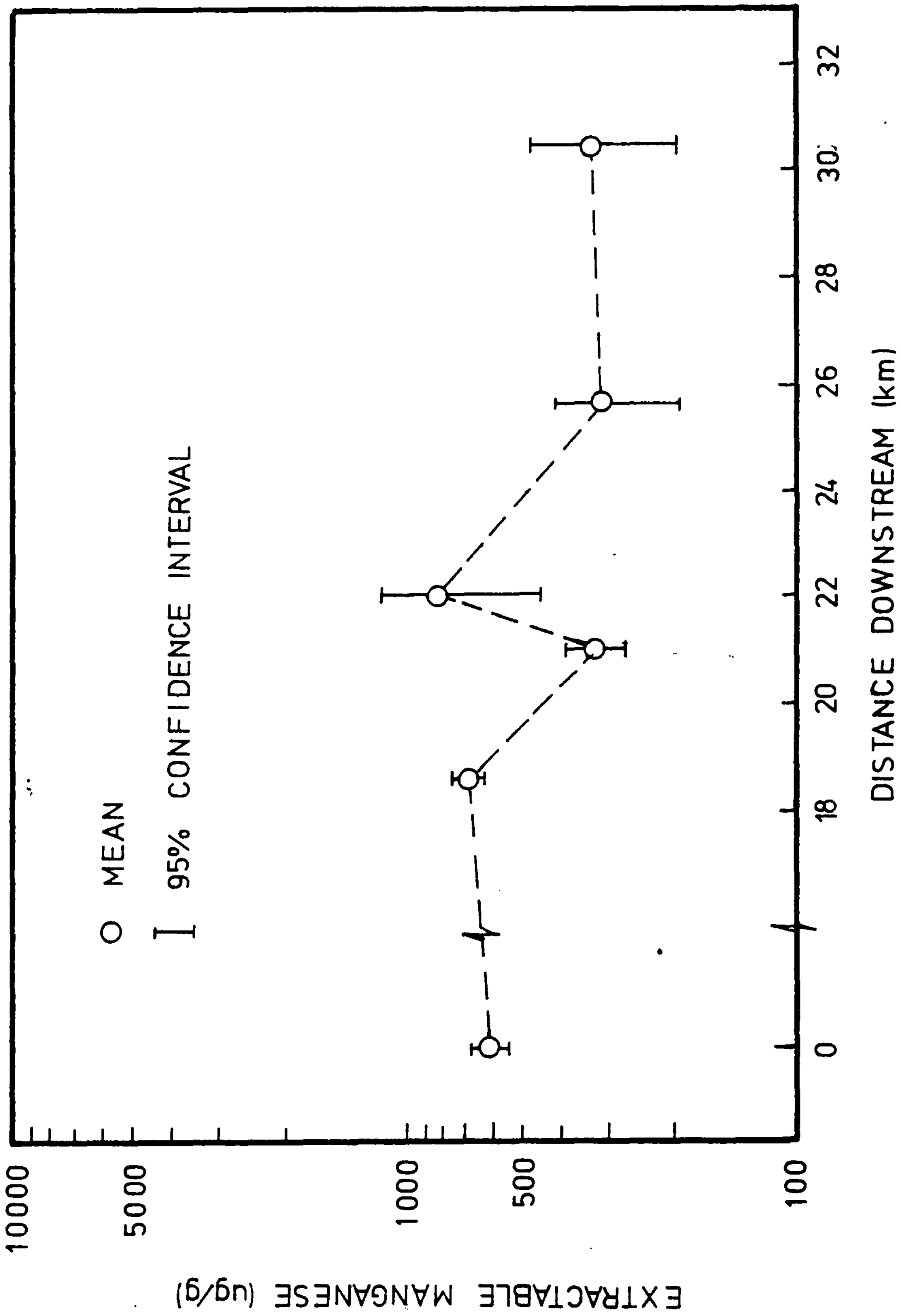

Figure D7. Extractable manganese in sediments from all six Bull Run stream stations.

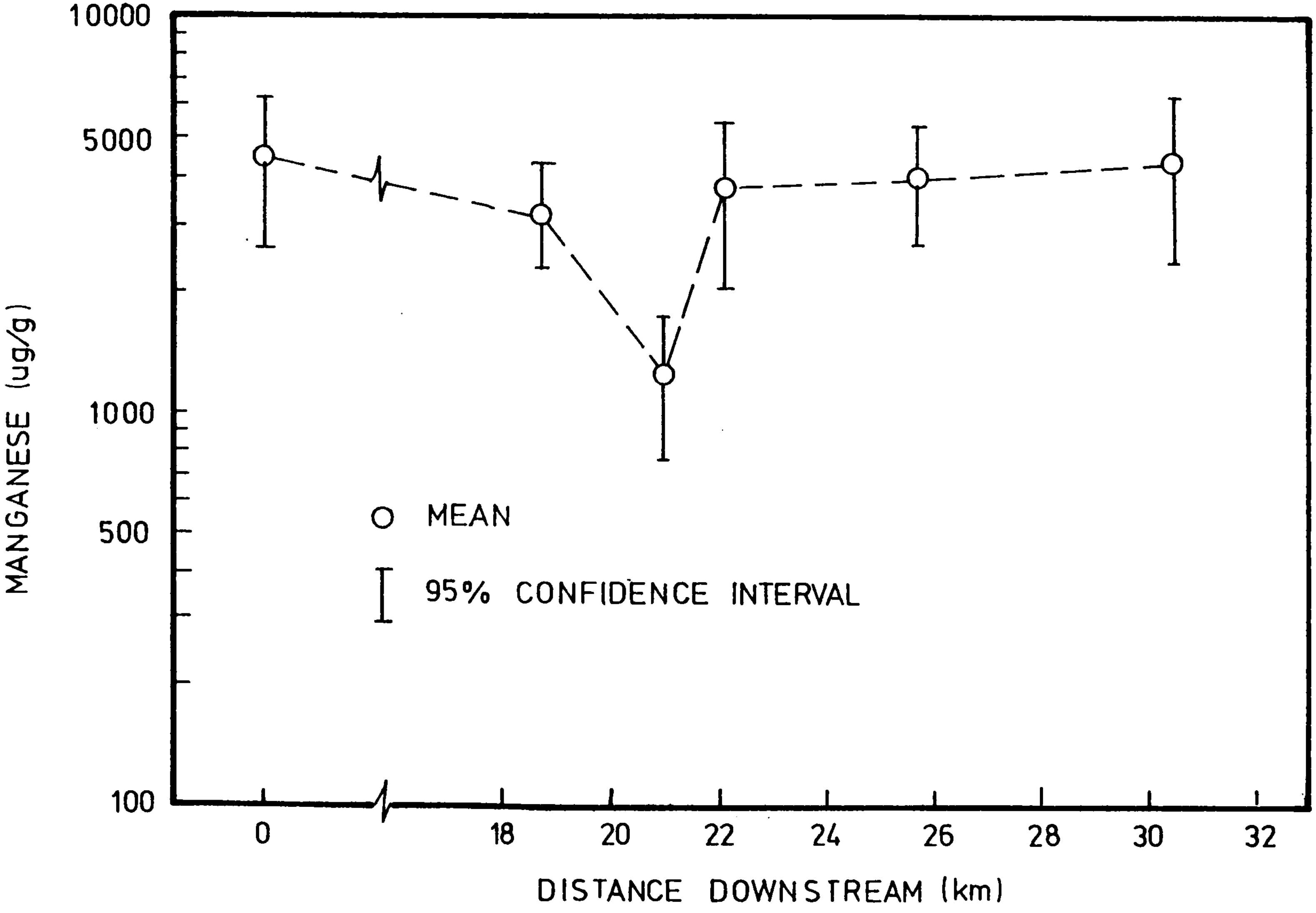

Figure D8. Manganese concentrations in detritus from all six Bull Run stream stations.

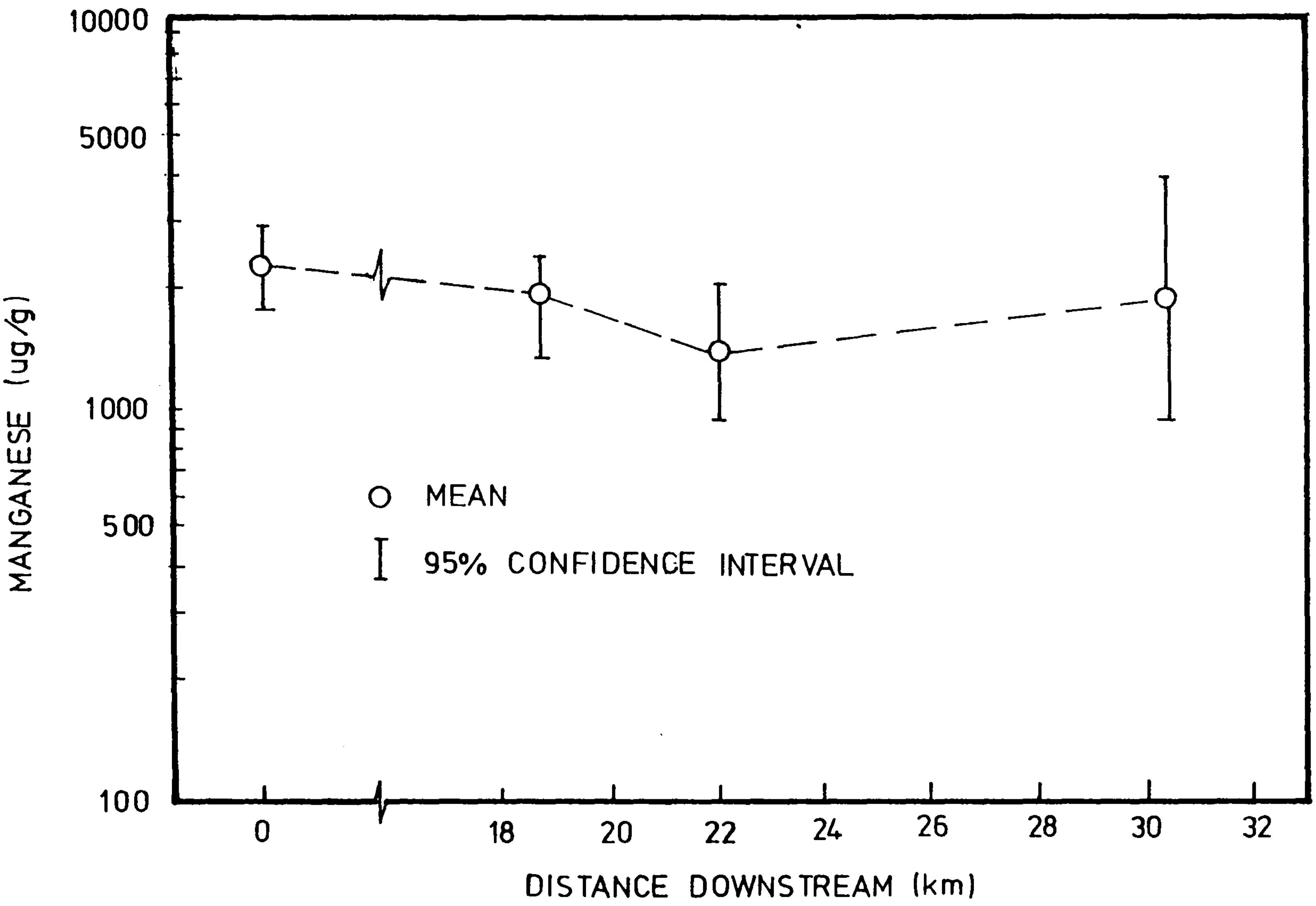

Figure D9. Manganese concentrations in caddisflies from Bull Run Stations 1, 2, 4, and 6.

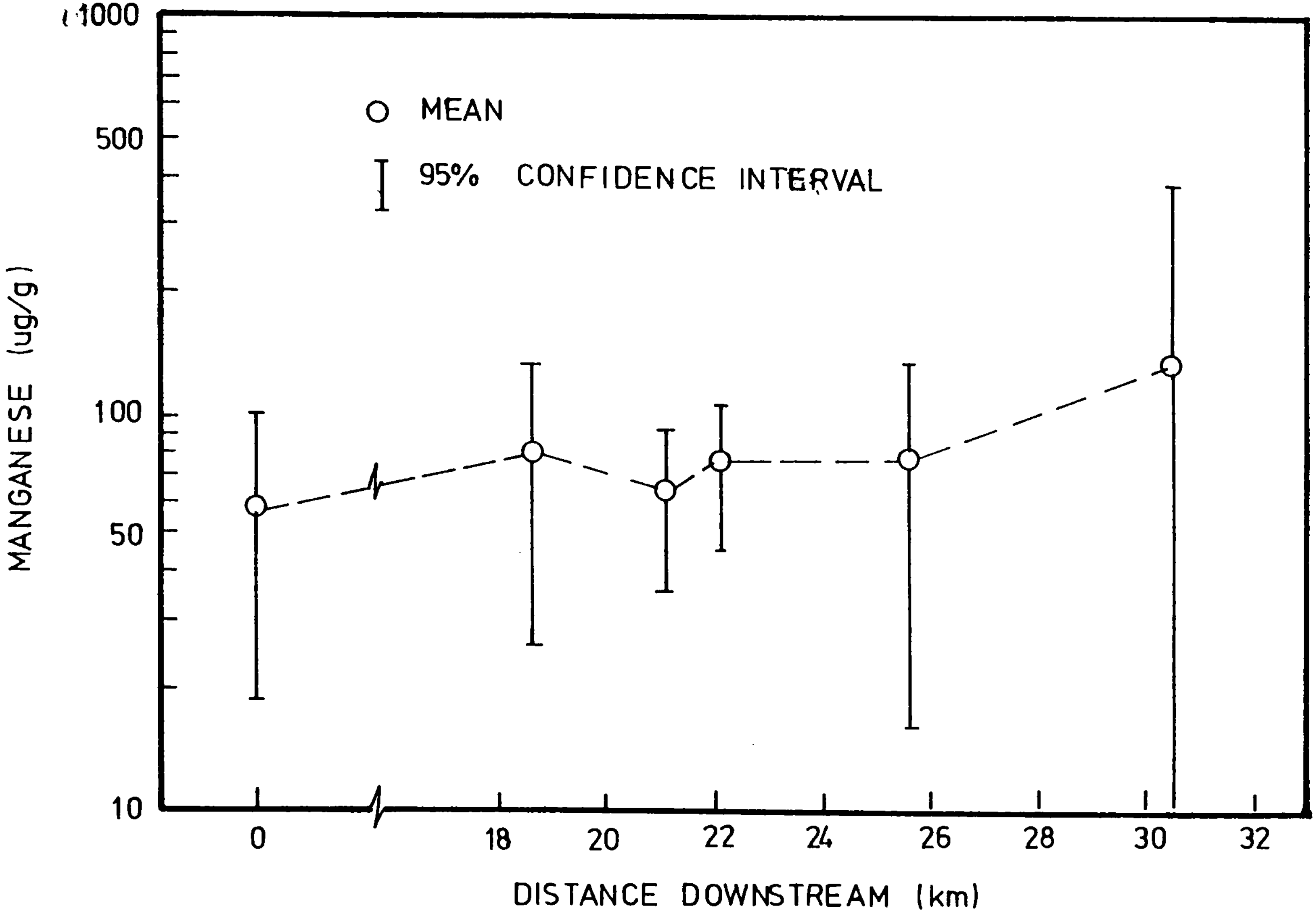

Figure D10. Manganese concentrations in crayfish from all six Bull Run stream stations.

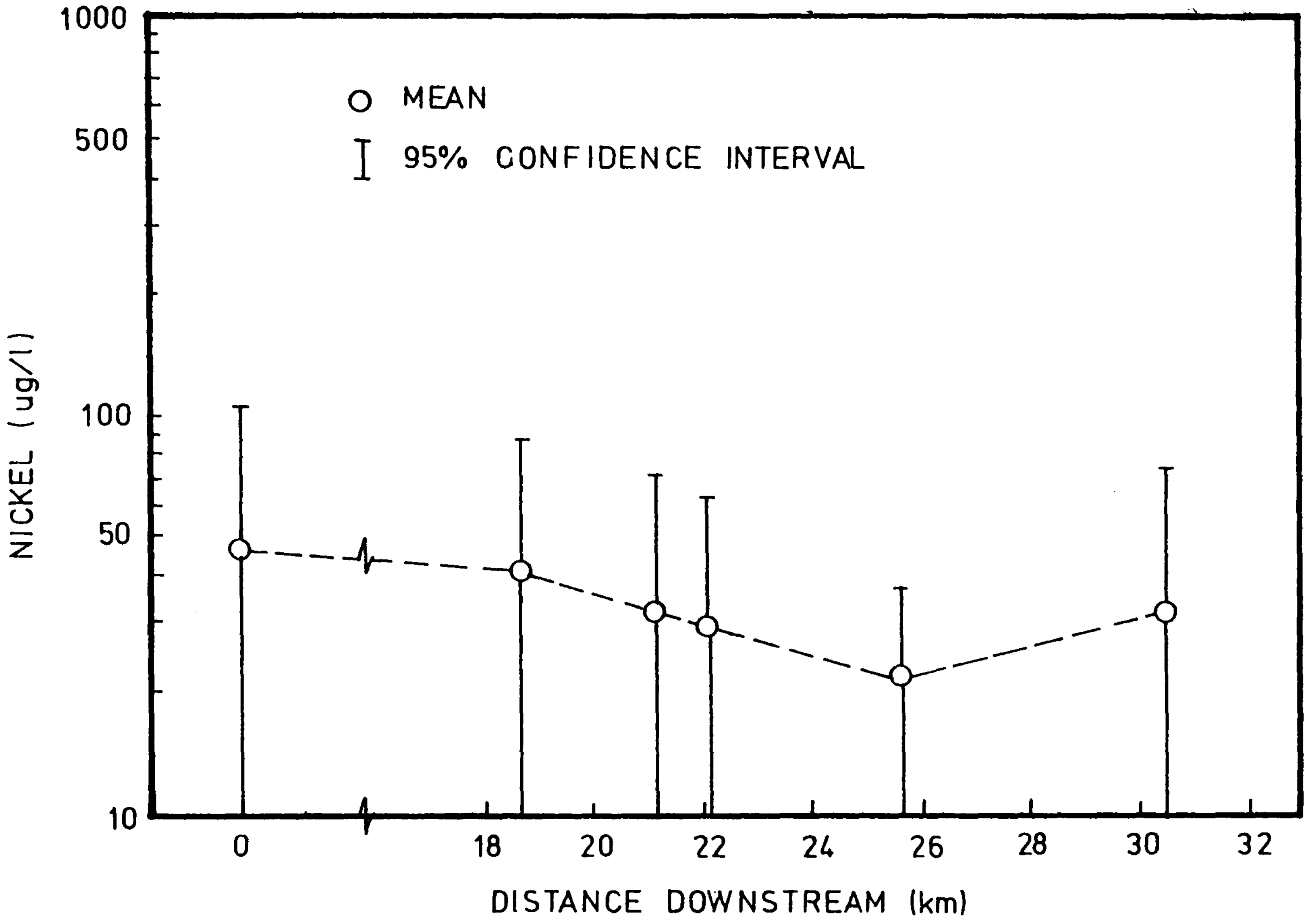

Figure D11. Total nickel concentrations in water at all six Bull Run stream stations.

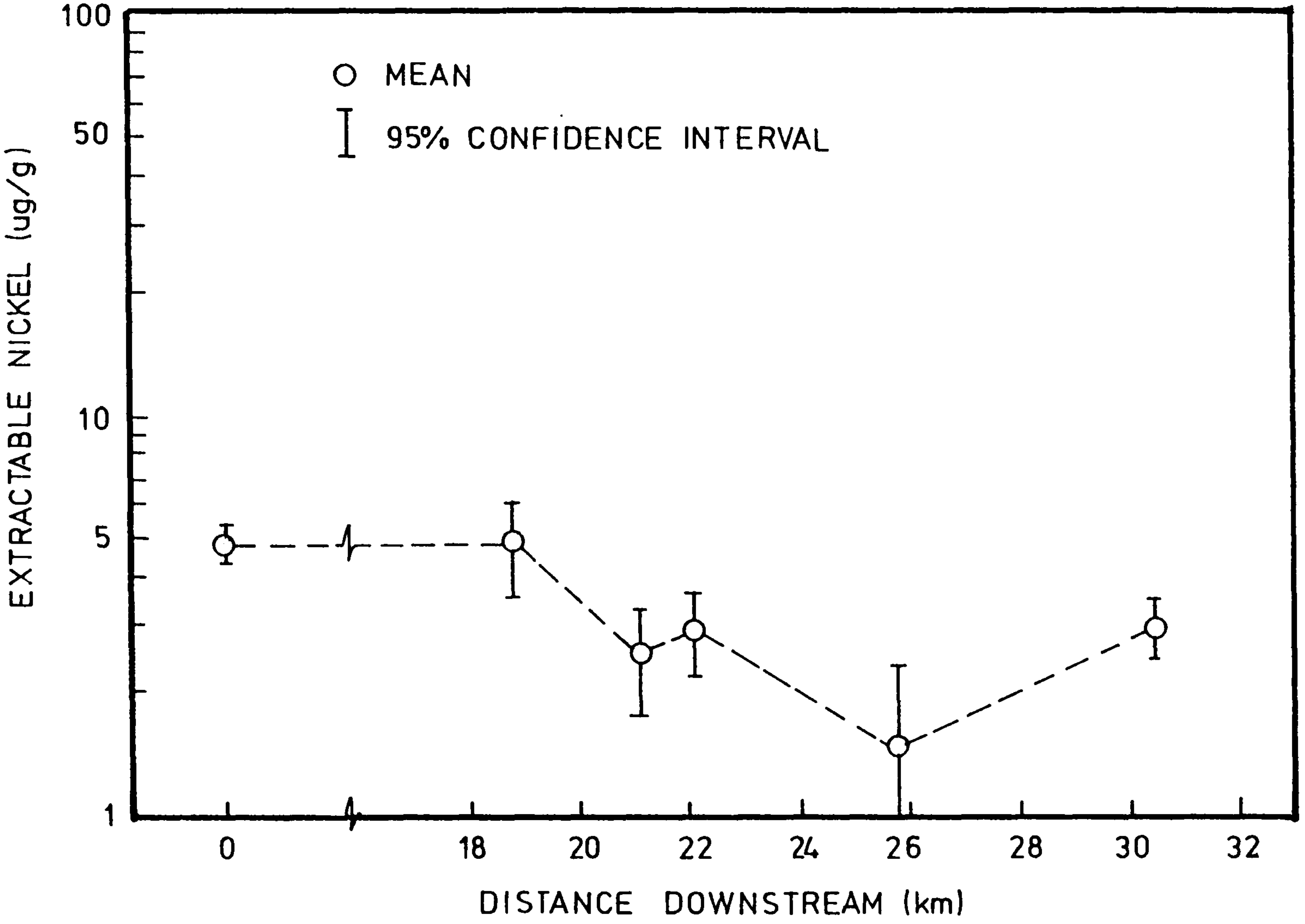

Figure D12. Extractable nickel in sediments from all six Bull Run stream stations.

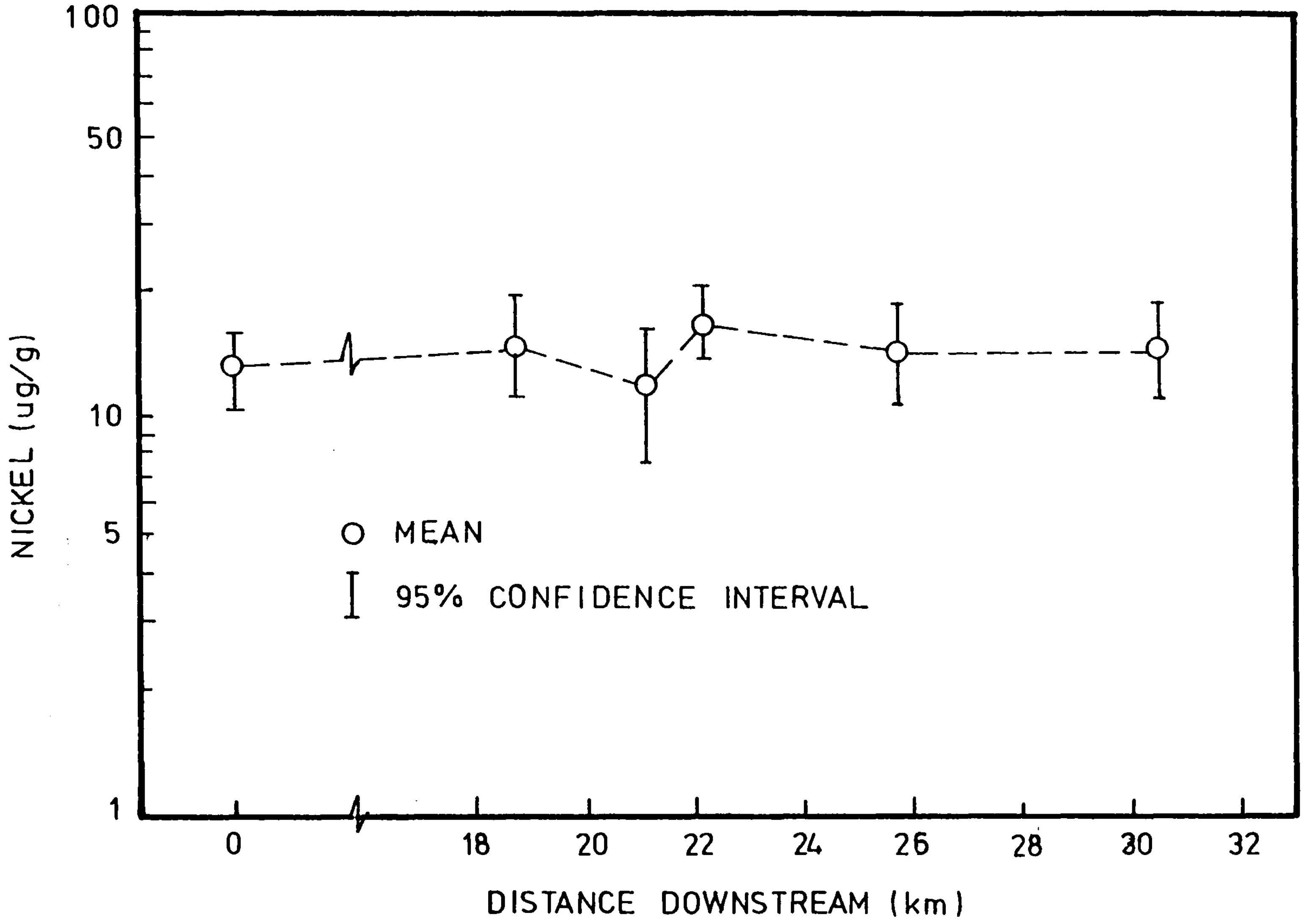

Figure D13. Nickel concentrations in detritus from all six Bull Run stream stations.

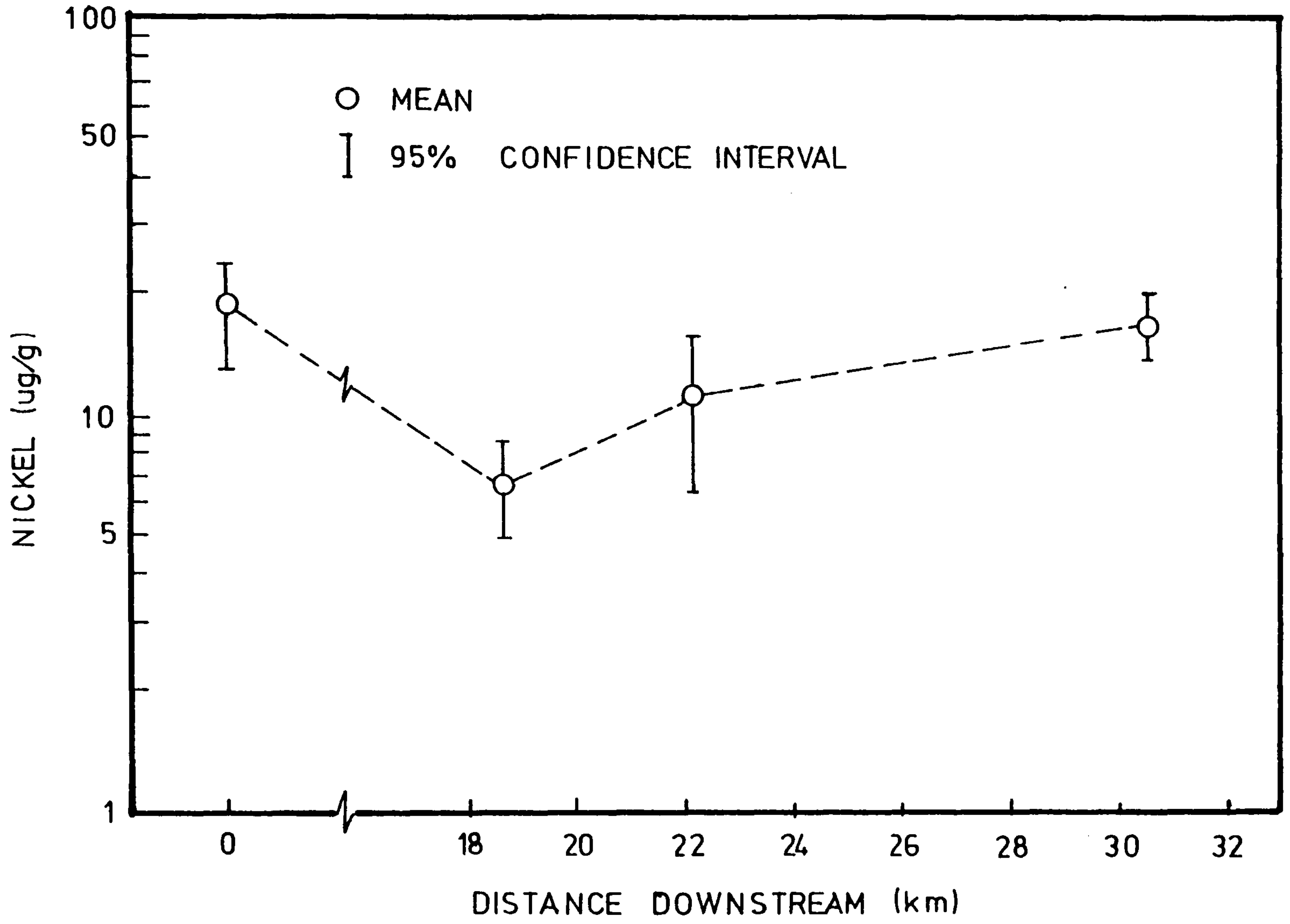

Figure D14. Nickel concentrations in caddisflies from Bull Run Stations 1, 2, 4, and 6.

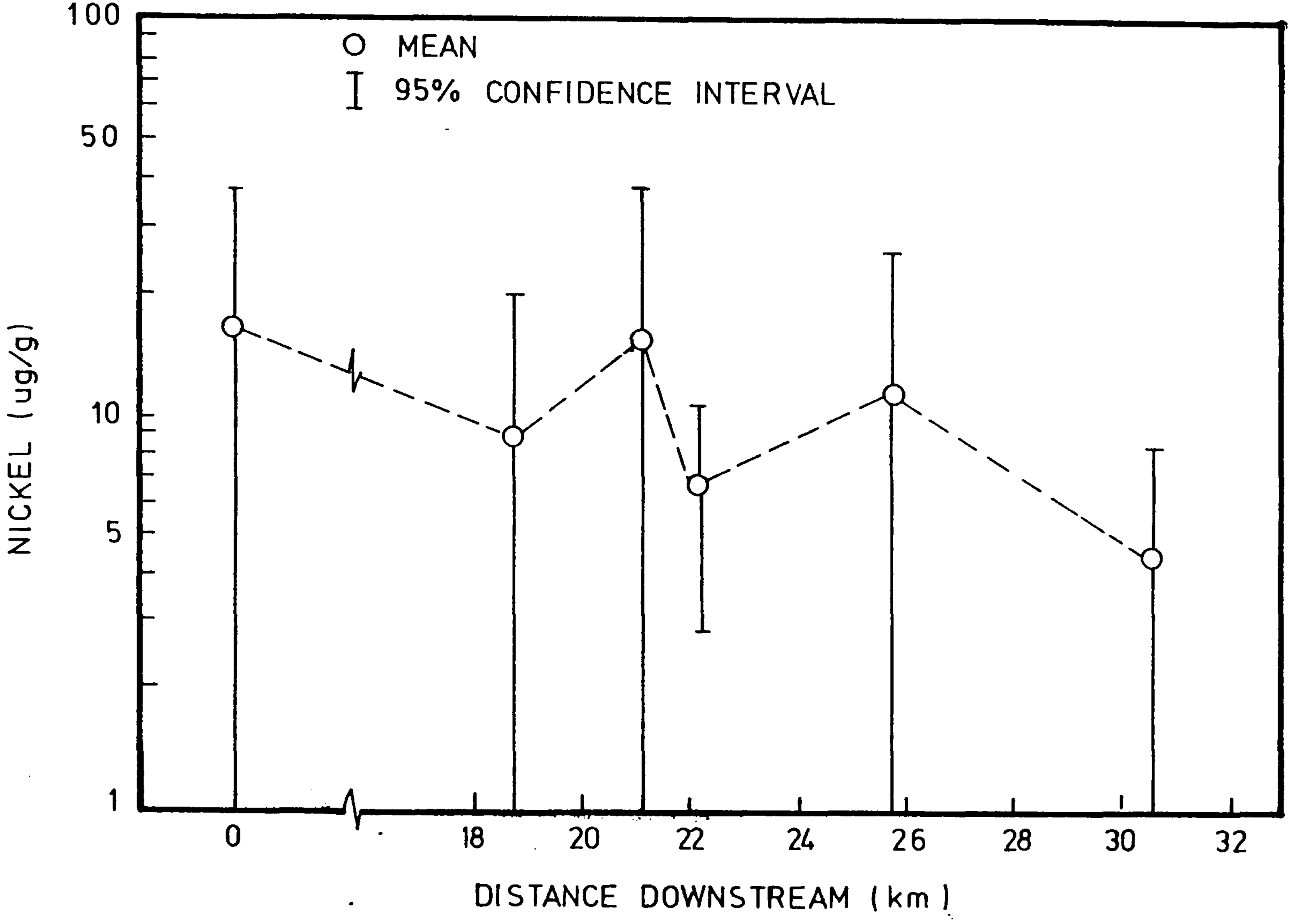

Figure D15. Nickel concentrations in crayfish from all six Bull Run stream stations.

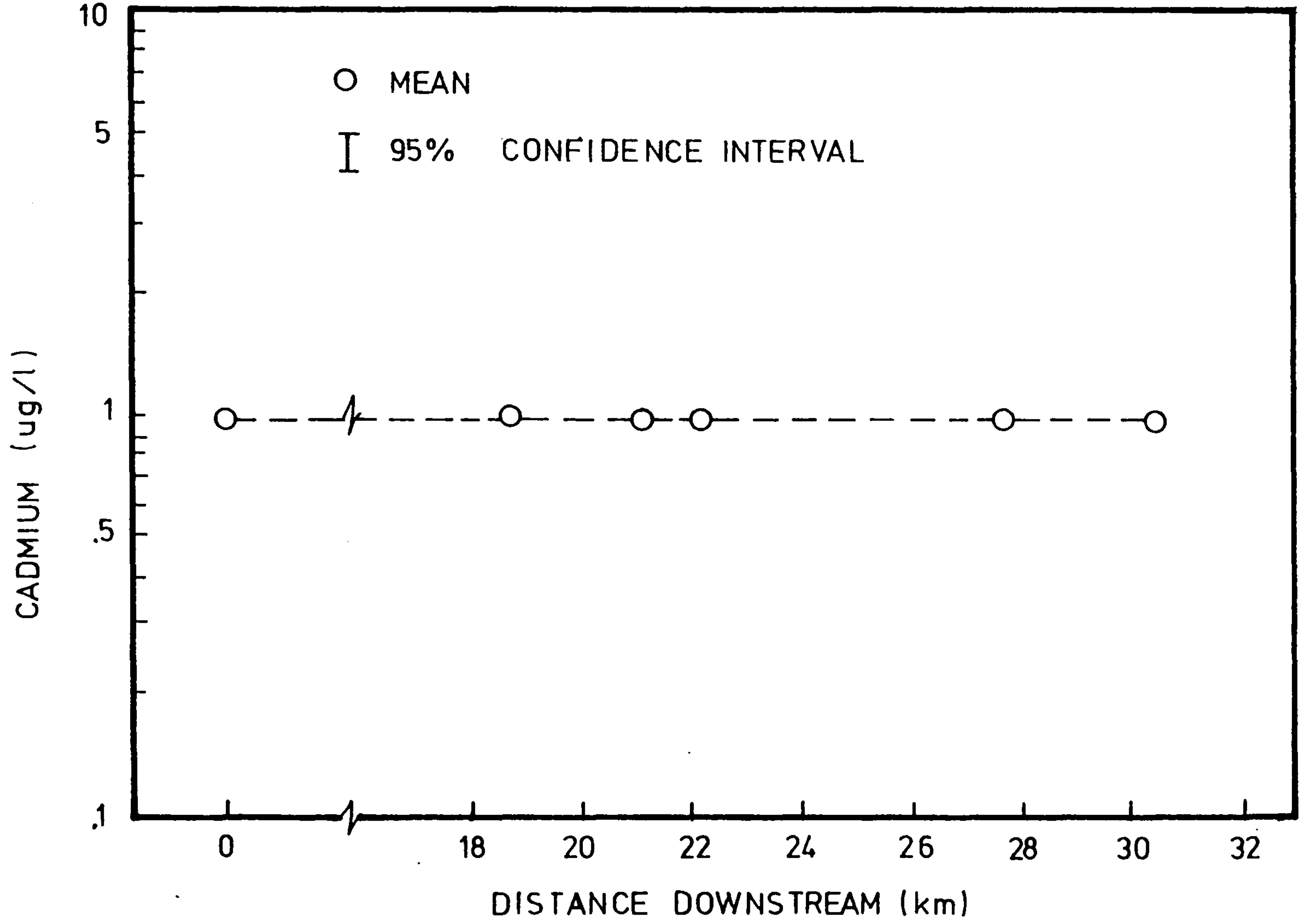

Figure D16. Total cadmium concentrations in water for all six Bull Run stream stations.

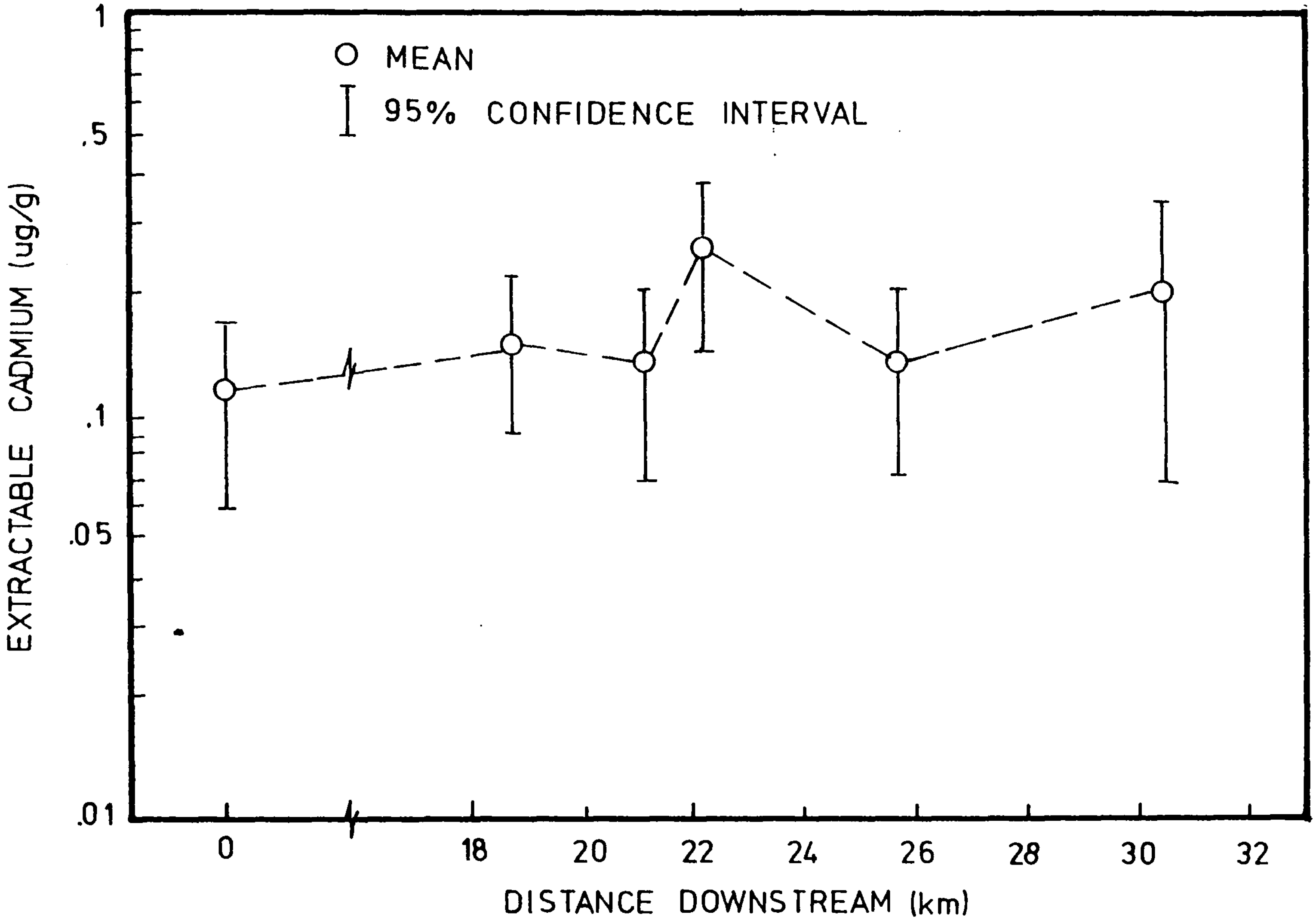

Figure D17. Extractable cadmium in sediments from all six Bull Run stream stations.

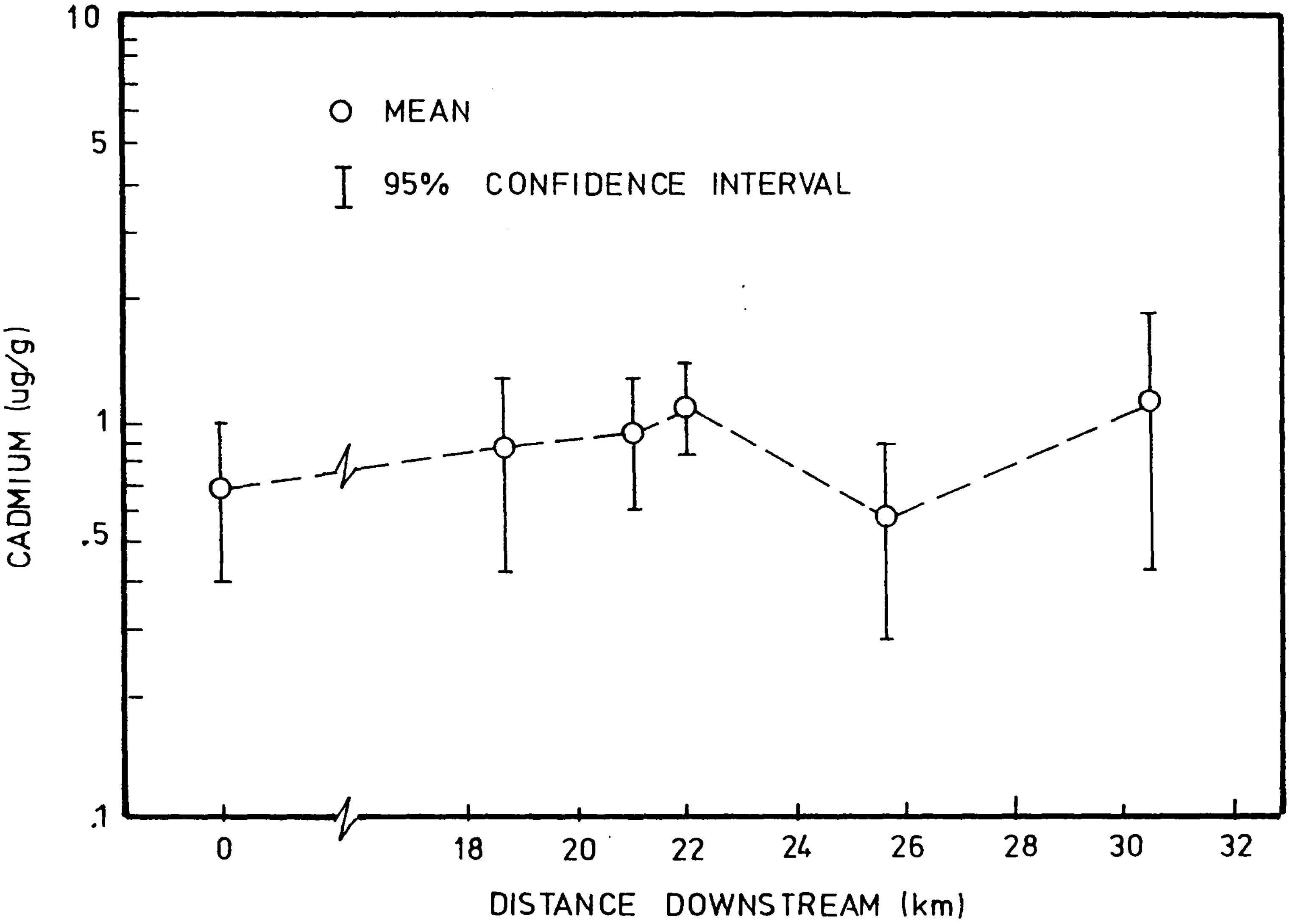

Figure D18. Cadmium concentrations in detritus from all six Bull Run stream stations.

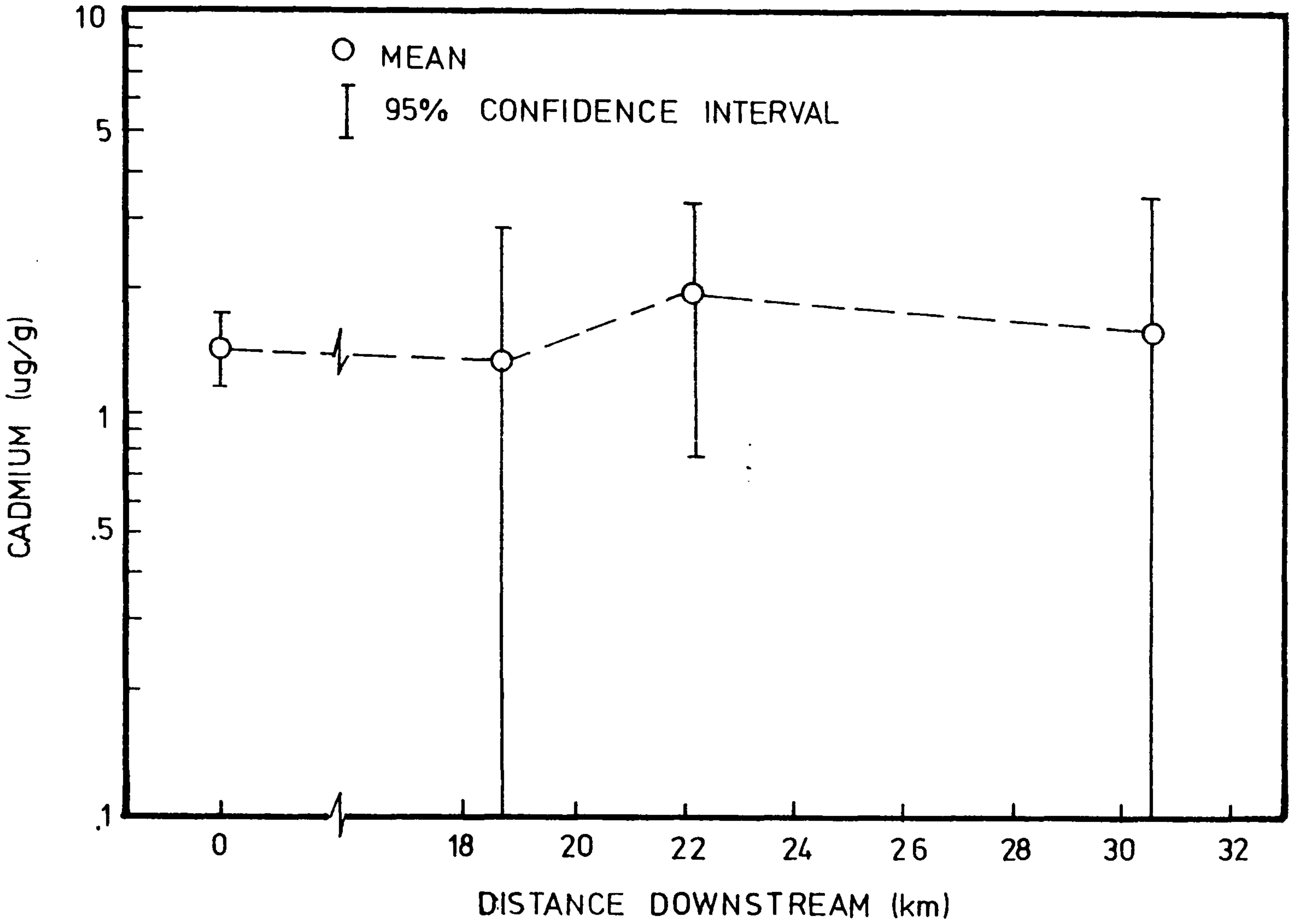

Figure D19. Cadmium concentrations in caddisflies from Bull Run Stations 1, 2, 4, and 6.

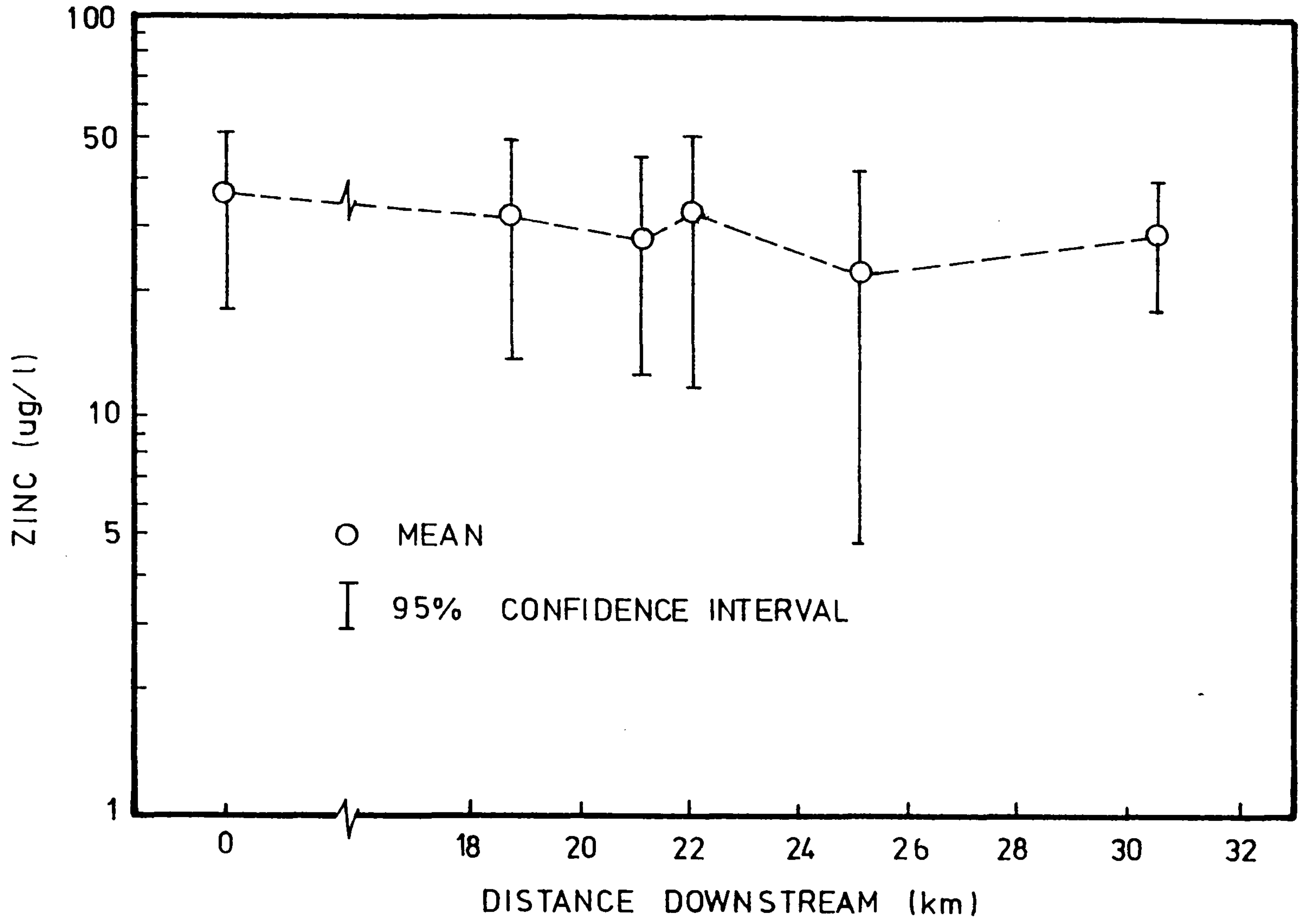

Figure D20. Total zinc concentrations in water at all six Bull Run stream stations.

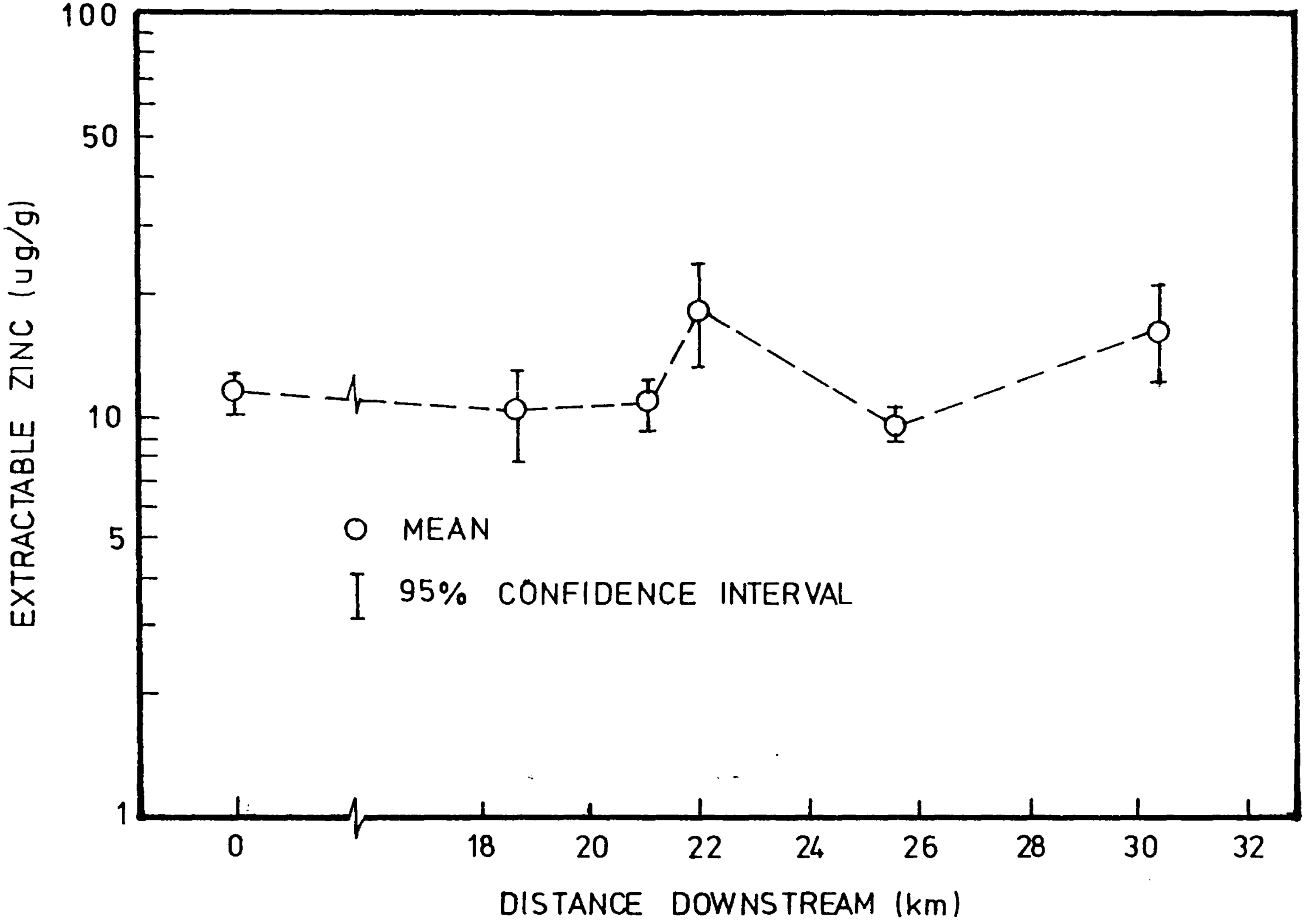

Figure D21. Extractable zinc in sediments from all six Bull Run stream stations.

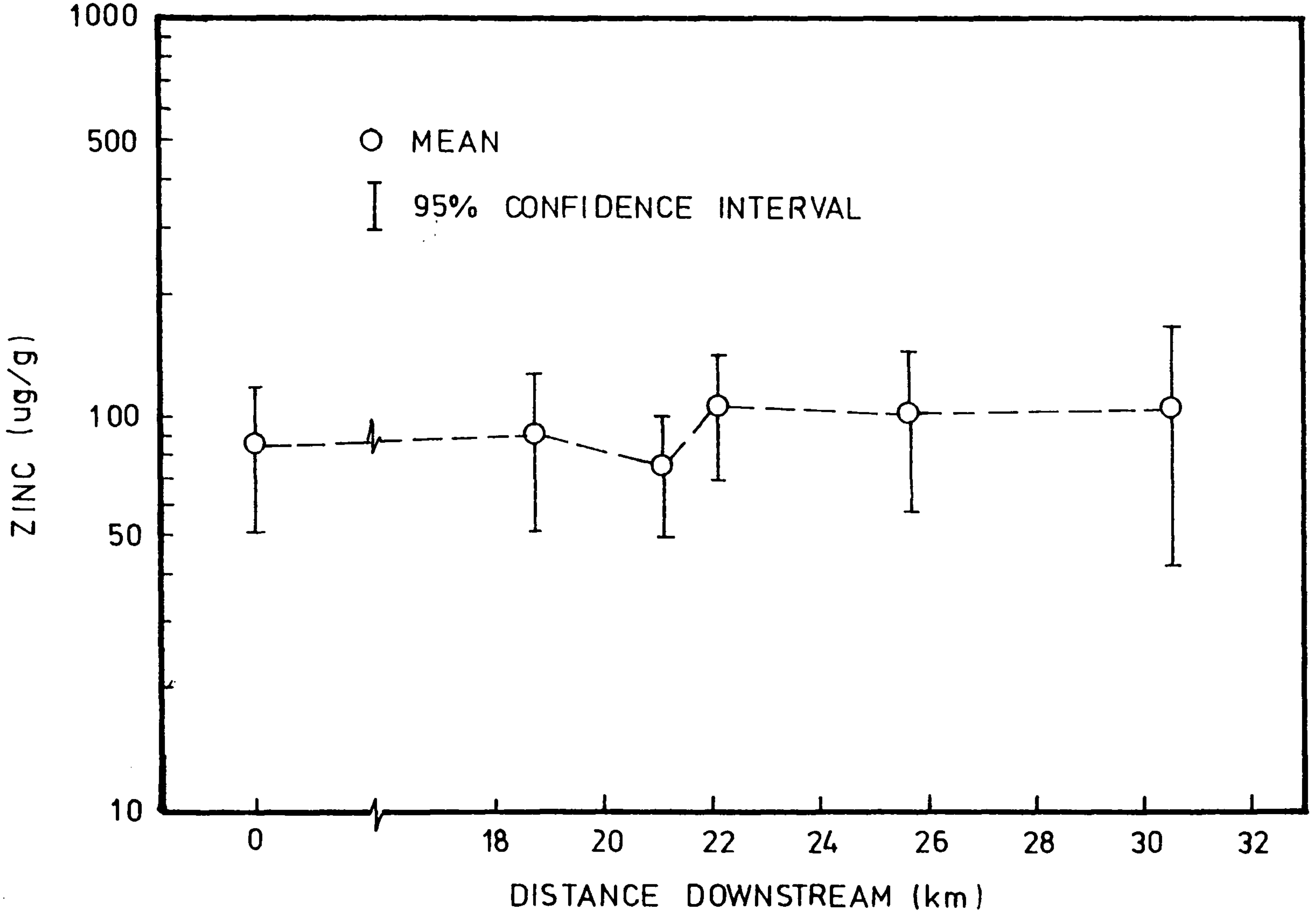

Figure D22. Zinc concentrations in detritus from all six Bull Run stream stations.

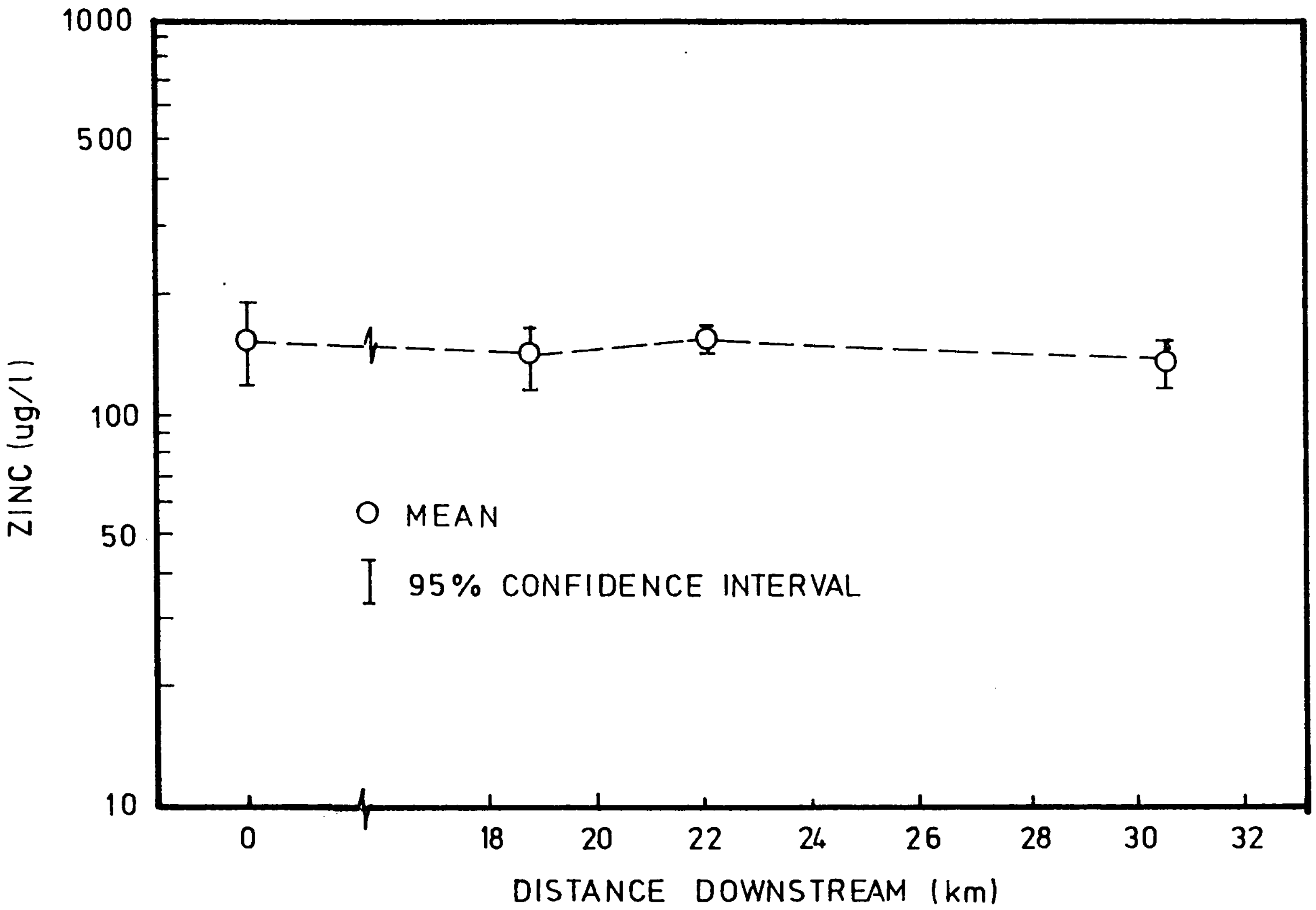

Figure D23. Zinc concentrations in caddisflies from Bull Run Stations 1, 2, 4, and 6.

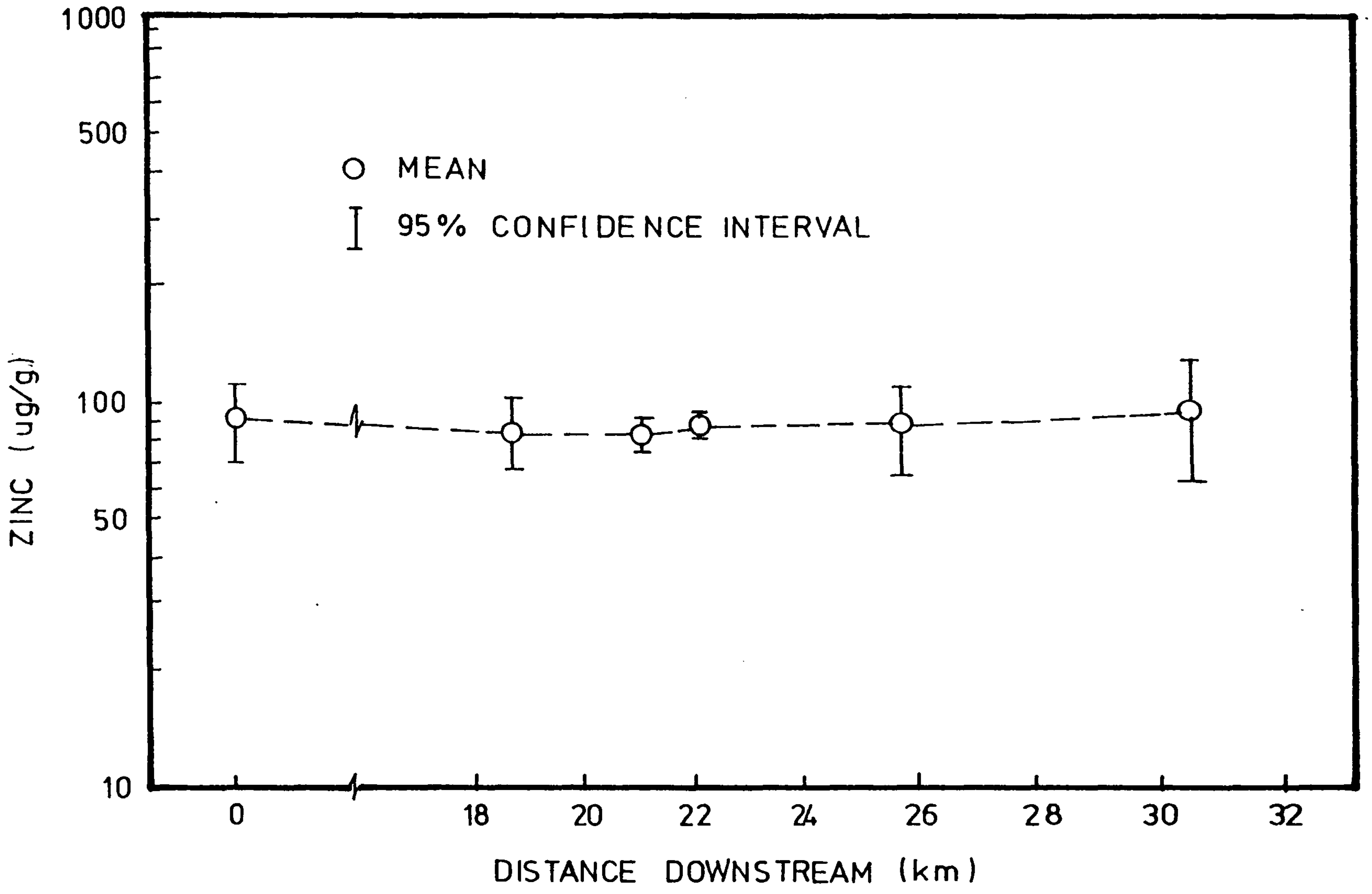

Figure D24. Zinc concentrations in crayfish from all six Bull Run stream stations.

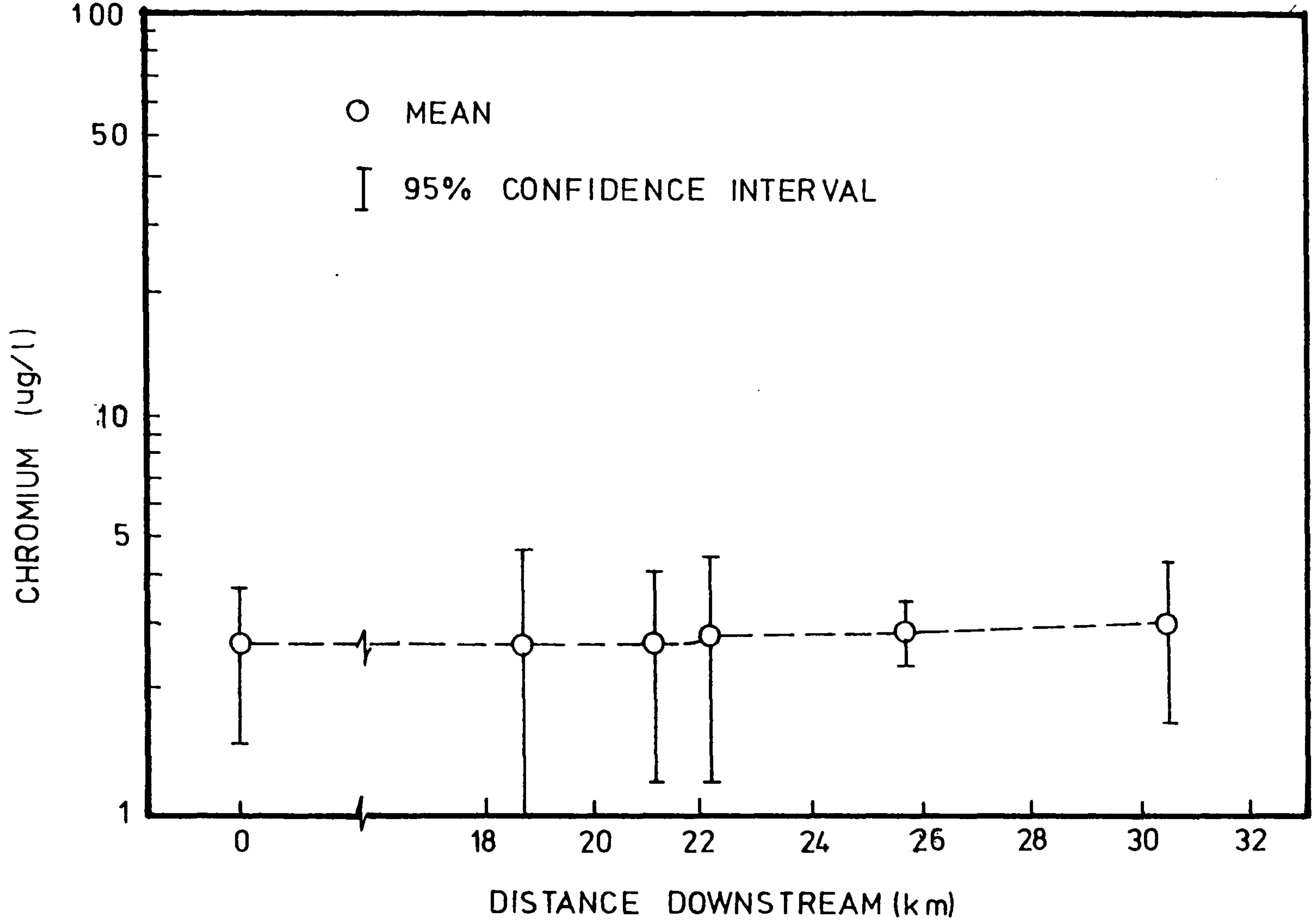

Figure D25. Total chromium concentrations in water at all six Bull Run stream stations.

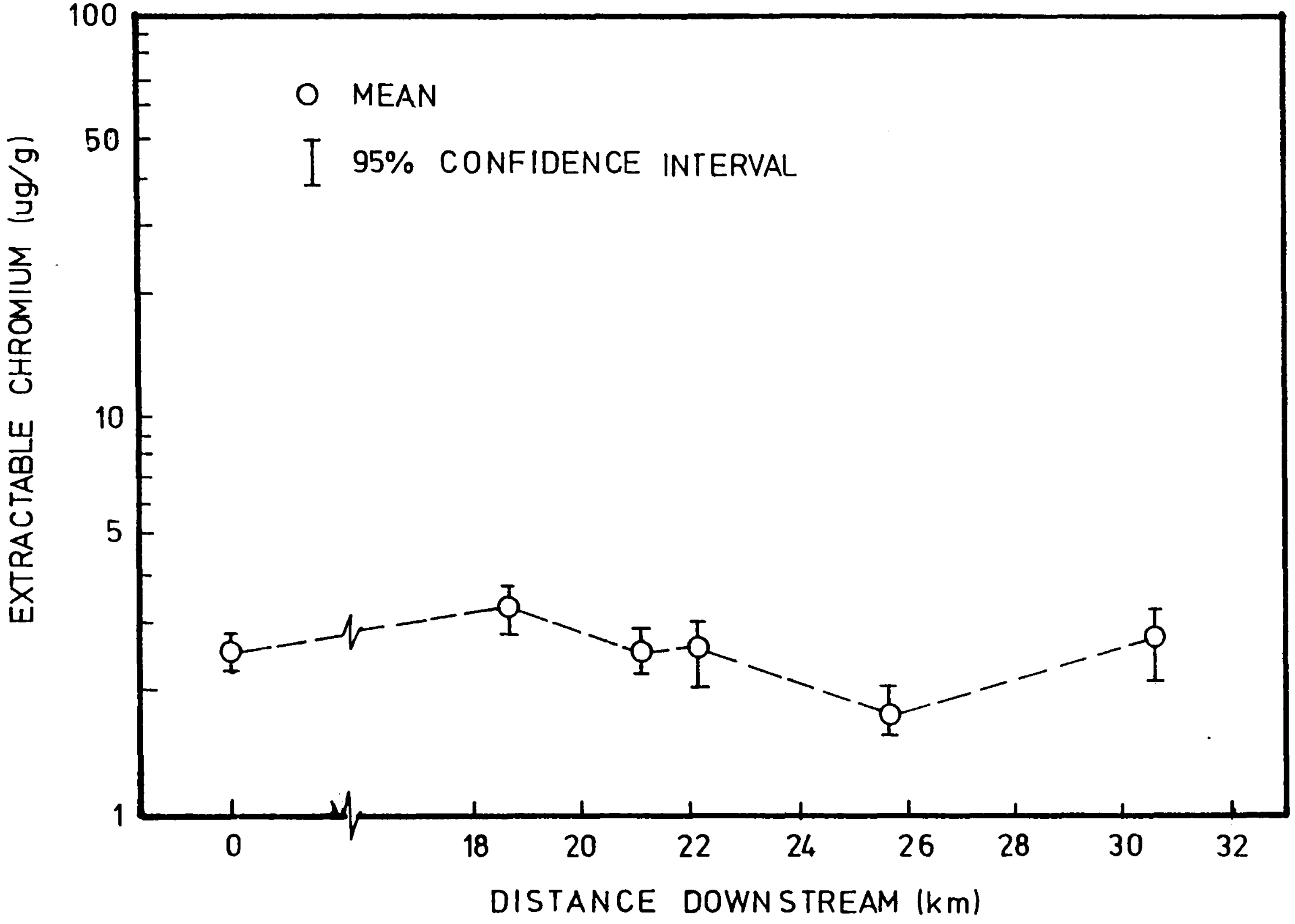

Figure D26. Extractable chromium in sediments from all six Bull Run stream stations.

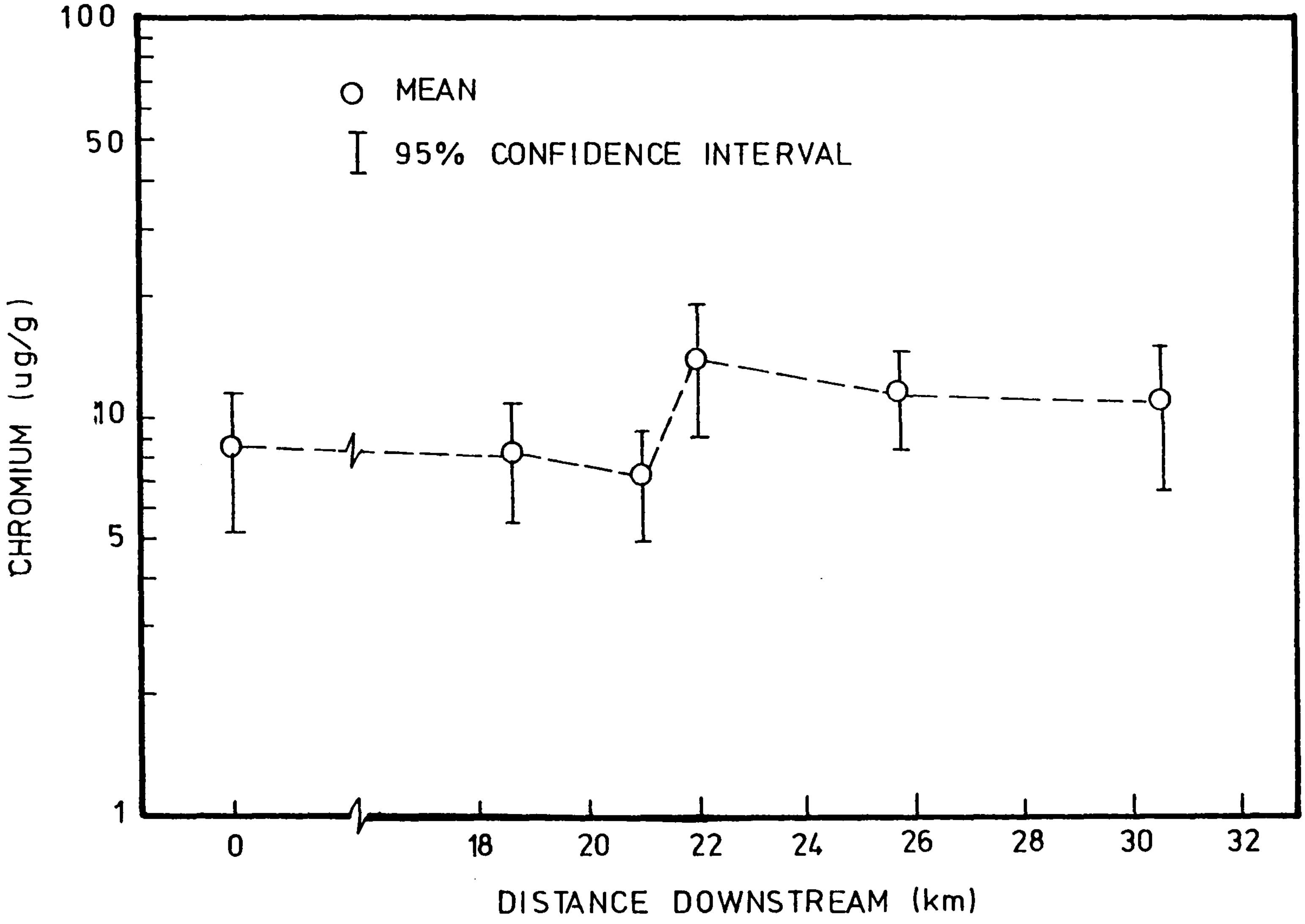

Figure D27. Chromium concentrations in detritus from all six Bull Run stream stations.

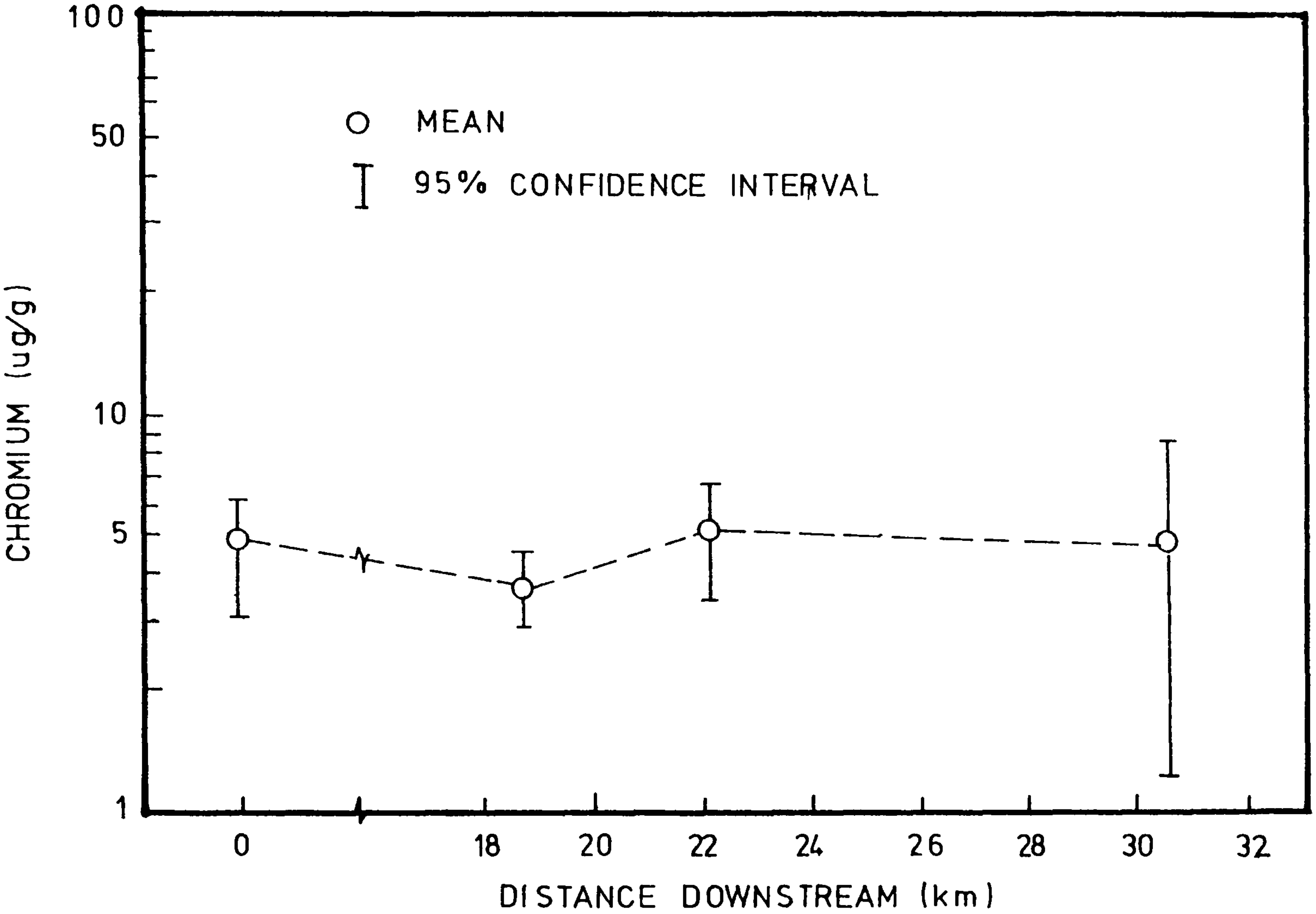

Figure D28. Chromium concentrations in caddisflies from Bull Run Stations 1, 2, 4, and 6.

Table E1

Mean Iron Concentrations for all Stream Components and the Results of Duncan's Multiple Range Analysis for Comparing Differences of These Means Among the Stream Stations

Stream Component	Stream Station and Corresponding Mean Iron Concentrations*					
Dissolved Iron, g/g	1	4	3	2	6	5
	180	167	163	135	128	116
Total Iron, g/l	1	6	2	3	4	5
	550	479	445	437	436	325
Sediment, g/g	2	1	4	3	6	5
	6,490	5,120	4,820	3,790	3,380	2,260
Detritus, g/g	4	5	1	2	6	3
	12,100	10,200	9,520	9,000	8,480	5,040
Caddisflies, g/g	6	1	2	4		
	4,540	4,360	3,610	3,600		
Snails, g/g	2	6				
	1,290	846				
Crayfish, g/g	1	4	3	2	5	6
	185	157	134	118	114	84.5

*Means connected by the same bracket are not significantly different from each other at the 0.95 level.

Table E2

Mean Manganese Concentrations for all Stream Components and the Results of Duncan's Multiple Range Analysis for Comparing Differences of These Means Among the Stream Stations

Stream Component	Stream Station and Corresponding Mean Manganese Concentrations*					
Dissolved Manganese µg/l	6	5	4	3	1	2
	206	161	132	52	47	38
Total Manganese, µg/l	6	5	1	2	4	3
	234	170	163	143	140	82
Sediment, µg/g	4	2	1	6	3	5
	815	699	606	335	330	309
Detritus, µg/g	1	6	5	4	2	3
	4,440	4,270	3,960	3,730	3,290	1,280
Caddisflies, µg/g	6	1	2	4		
	2,450	2,340	1,970	1,450		
Snails, µg/g	2	6				
	586	319				
Crayfish, µg/g	6	2	5	4	3	1
	135	81.5	77.6	75.6	63.7	58.5

*Means connected by the same bracket are not significantly different from each other at the 0.95 level.

Table E3

Mean Nickel Concentrations for all Stream Components and the Results of Duncan's Multiple Range Analysis for Comparing Differences of These Means Among the Stream Stations

Stream Component	Stream Station and Corresponding Mean Nickel Concentrations*					
Dissolved Nickel, μg/l	5	4	6	1	2	3
	7	6	3	3	2	2
Total Nickel, μg/l	1	2	3	6	4	5
	48	41	32	32	29	22
Sediment, μg/g	2	1	6	4	3	5
	4.9	4.8	3.0	2.9	2.5	1.5
Detritus, μg/g	4	2	6	5	1	3
	17.6	15.7	15.3	15.2	13.7	12.3
Caddisflies, μg/g	1	6	4	2		
	19.1	17.9	11.8	6.9		
Snails, μg/g	2	6				
	5.7	5.7				
Crayfish, μg/g	1	3	5	2	4	6
	17.1	16.6	10.8	9.0	6.9	4.6

*Means connected by the same bracket are not significantly different from each other at the 0.95 level.

Table E4

Meam Cadmium Concentrations for all Stream Components and the Results of Duncan's Multiple Range Analysis for Comparing Differences of These Means Among the Stream Stations

Stream Component	Stream Station and Corresponding Mean Cadmium Concentration*					
Dissolved Cadmium, µg/l	1	2	3	4	5	6
	1	1	1	1	1	1
Total Cadmium, µg/l	1	2	3	4	5	6
	1	1	1	1	1	1
Sediment, µg/g	4	6	2	3	5	1
	0.3	0.2	0.2	0.1	0.1	0.1
Detritus, µg/g	6	4	3	2	1	5
	1.2	1.1	0.9	0.9	0.7	0.6
Caddisflies, µg/g	4	6	1	2		
	2.0	1.7	1.5	1.4		
Snails, µg/g	6	2				
	1.7	1.3				
Crayfish, µg/g	1	2	3	4	5	6
	0	0	0	0	0	0

*Means connected by the same bracket are not significantly different from each other at the 0.95 level.

Table E5

Mean Zinc Concentrations for all Stream Components and the Results of Duncan's Multiple Range Analysis for Comparing Differences of These Means Among the Stream Stations

Stream Component	Stream Station and Corresponding Mean Zinc Concentration*					
Dissolved Zinc, µg/l	1	2	4	3	6	5
	23	16	15	13	12	11
Total Zinc, µg/l	1	4	2	6	3	5
	36	32	32	29	28	24
Sediment, µg/g	4	6	1	3	2	5
	18.4	17.0	11.6	11.0	10.4	9.7
Detritus, µg/g	4	6	5	2	1	3
	109	108	105	91.7	85.8	78.2
Caddisflies, µg/g	4	1	2	6		
	164	161	150	144		
Snails, µg/g	6	2				
	104	94.7				
Crayfish, µg/g	6	1	5	4	2	3
	96.4	91.7	91.1	89.4	85.9	83.2

*Means connected by the same bracket are not significantly different from each other at the 0.95 level.

Table E6

Mean Chromium Concentrations for all Stream Components and the Results of Duncan's Multiple Range Analysis for Comparing Differences of These Means Among the Stream Station

Stream Component	Stream Station and Corresponding Mean Chromium Concentration*					
Dissolved Chromium µg/l	5	6	4	1	2	3
	2	2	2	1	1	1
Total Chromium µg/l	6	4	5	1	2	3
	3	3	3	3	3	3
Sediment, µg/g	2	6	3	4	1	5
	3.3	2.8	2.6	2.6	2.5	1.8
Detritus, µg/g	4	5	6	1	2	3
	14.2	11.7	11.0	8.6	8.1	7.2
Caddisflies, µg/g	4	1	6	2		
	5.1	4.9	4.7	3.7		
Snails, µg/g	2	6				
	2.3	1.7				
Crayfish, µg/g	1	2	3	4	5	6
	0	0	0	0	0	0

*Means connected by the same bracket are not significantly different from each other at the 0.95 level.

Table F1

Correlation Coefficients Derived From Comparisons of Iron Concentrations Among the Various Stream Components

Components	Total Iron in Water	Dissolved Iron in Water	Sediment	Detritus	Caddisflies	Snails	Crayfish
Total Iron in Water	1.00 (29)	0.68** (29)	0.07 (29)	-0.02 (29)	-0.06 (17)	-0.44 (9)	0.21 (29)
Dissolved Iron in Water	0.68** (29)	1.00 (29)	-0.01 (29)	0.07 (29)	-0.09 (17)	-0.49 (9)	0.55** (29)
Sediment	0.07 (29)	-0.01 (29)	1.00 (29)	0.06 (29)	-0.10 (17)	0.41 (9)	0.25 (29)
Detritus	-0.02 (29)	0.07 (29)	0.06 (29)	1.00 (29)	-0.56* (17)	-0.45 (9)	0.14 (29)
Caddisflies	-0.06 (17)	-0.09 (17)	-0.10 (17)	-0.56* (17)	1.00 (17)	-0.00 (7)	0.03 (17)
Snails	-0.44 (9)	-0.49 (9)	0.41 (9)	-0.45 (9)	-0.00 (7)	1.00 (9)	0.33 (9)
Crayfish	0.21 (29)	0.55** (29)	0.25 (29)	0.14 (29)	0.03 (17)	0.33 (9)	1.00 (29)

*Significant at the 0.95 confidence level.

**Significant at the 0.99 confidence level.

( )Number of observations.

Table F2

Correlation Coefficients Derived From Comparisons of Manganese Concentrations Among the Various Stream Components

Component	Total Manganese in Water	Dissolved Manganese in Water	Sediment	Detritus	Caddisflies	Snails	Crayfish
Total Manganese in Water	1.00 (29)	0.68** (29)	-0.14 (29)	0.37* (29)	-0.06 (17)	-0.21 (9)	0.29 (29)
Dissolved Manganese in Water	0.68** (29)	1.00 (29)	-0.30 (29)	0.29 (29)	-0.15 (17)	-0.58 (9)	0.25 (29)
Sediment	-0.14 (29)	-0.30 (29)	1.00 (29)	0.21 (29)	-0.16 (17)	0.68* (9)	0.06 (29)
Detritus	0.37* (29)	0.29 (29)	0.21 (29)	1.00 (29)	0.17 (17)	-0.17 (9)	0.21 (29)
Caddisflies	-0.06 (17)	-0.15 (17)	-0.16 (17)	0.17 (17)	1.00 (17)	-0.32 (7)	0.33 (17)
Snails	-0.21 (9)	-0.58 (9)	0.68* (9)	-0.17 (9)	-0.32 (7)	1.00 (9)	-0.30 (9)
Crayfish	0.29 (29)	0.25 (29)	0.06 (29)	0.21 (29)	0.33 (17)	-0.30 (9)	1.00 (29)

*Significant at the 0.95 confidence level.

**Significant at the 0.99 confidence level.

()Number of observations.

Table F3

Correlation Coefficients Derived From Comparisons of Nickel Concentrations Among the Various Stream Components

Component	Total Nickel in Water	Dissolved Nickel in Water	Sediment	Detritus	Caddisflies	Snails	Crayfish
Total Nickel in Water	1.00 (29)	-0.51** (29)	0.36 (29)	0.20 (29)	-0.03 (17)	-0.71* (9)	-0.02 (29)
Dissolved Nickel in Water	-0.51** (29)	1.00 (29)	-0.45* (29)	0.09 (29)	-0.04 (17)	0.34 (9)	0.19 (29)
Sediment	0.36 (29)	-0.45* (29)	1.00 (29)	0.04 (29)	-0.07 (17)	0.04 (9)	-0.05 (29)
Detritus	0.20 (29)	0.09 (29)	0.04 (29)	1.00 (29)	-0.37 (17)	0.03 (9)	0.16 (29)
Caddisflies	-0.03 (17)	-0.04 (17)	-0.07 (17)	-0.37 (17)	1.00 (17)	0.09 (7)	0.16 (17)
Snails	-0.71* (9)	0.34 (9)	0.04 (9)	0.03 (9)	0.09 (7)	1.00 (9)	-0.19 (9)
Crayfish	-0.02 (29)	0.19 (29)	-0.05 (29)	0.16 (29)	0.16 (17)	-0.19 (9)	1.00 (29)

*Significant at the 0.95 confidence level.

**Significant at the 0.99 confidence level.

( )Number of observations.

Table F4

Correlation Coefficients Derived From Comparisons of Cadmium Concentrations Among the Various Stream Components

Components	Sediment	Detritus	Caddisflies	Snails
Sediment	1.00 (29)	0.29 (29)	0.24 (17)	-0.08 (9)
Detritus	0.29 (29)	1.00 (29)	0.09 (17)	0.21 (9)
Caddisflies	0.24 (17)	0.09 (17)	1.00 (17)	0.02 (7)
Snails	-0.08 (9)	0.21 (9)	0.02 (7)	1.00 (9)

*Significant at the 0.95 confidence level.

**Significant at the 0.99 confidence level.

() Number of Observations.

Table F5

Correlation Coefficients Derived From Comparisons of Zinc Concentrations Among the Various Stream Components

Component	Total Zinc in Water	Dissolved Zinc in Water	Sediment	Detritus	Caddisflies	Snails	Crayfish
Total Zinc in Water	1.00 (29)	0.25 (29)	0.06 (29)	-0.07 (29)	-0.14 (17)	0.31 (9)	-0.11 (29)
Dissolved Zinc in Water	0.25 (29)	1.00 (29)	-0.01 (29)	-0.26 (29)	0.29 (17)	-0.59 (9)	-0.08 (29)
Sediment	0.06 (29)	-0.01 (29)	1.00 (29)	0.21 (29)	0.05 (17)	0.40 (9)	0.20 (29)
Detritus	-0.07 (29)	-0.26 (29)	0.21 (29)	1.00 (29)	-0.27 (17)	0.80** (9)	-0.14 (29)
Caddisflies	-0.14 (17)	0.29 (17)	0.05 (17)	-0.27 (17)	1.00 (17)	-0.75 (7)	0.13 (17)
Snails	0.31 (9)	-0.59 (9)	0.40 (9)	0.80** (9)	-0.75 (7)	1.00 (9)	0.18 (9)
Crayfish	-0.11 (29)	-0.08 (29)	0.20 (29)	-0.14 (29)	0.13 (17)	0.18 (9)	1.00 (29)

*Significant at the 0.95 confidence level.

**Significant at the 0.99 confidence level.

()Number of observations.

Table F6

Correlation Coefficients Derived From Comparisons of Chromium Concentrations Among the Various Stream Components

Component	Total Chromium in Water	Dissolved Chromium in Water	Sediment	Detritus	Caddisflies	Snails
Total Chromium in Water	1.00 (29)	-0.22 (29)	0.15 (29)	0.14 (29)	-0.14 (17)	-0.47 (9)
Dissolved Chromium in Water	-0.22 (29)	1.00 (29)	-0.29 (29)	0.08 (29)	0.47 (17)	-0.24 (9)
Sediment	0.15 (29)	-0.29 (29)	1.00 (29)	-0.17 (29)	-0.13 (17)	0.08 (9)
Detritus	0.14 (29)	0.08 (29)	-0.17 (29)	1.00 (29)	-0.09 (17)	-0.85** (9)
Caddisflies	-0.14 (T7)	0.47 (17)	-0.13 (17)	-0.09 (17)	1.00 (17)	0.05 (7)
Snails	-0.47 (9)	-0.24 (9)	0.08 (9)	-0.85** (9)	0.05 (7)	1.00 (9)

*Significant at the 0.95 confidence level.

**Significant at the 0.99 confidence level.

()Number of observations.

Table G1

Metal Concentration and Carapace Length for Crayfish

Designation*	Carapace (mm)	Metal Concentration, µg/g							
		Fe	Mn	Ni	Pb	Cd	Zn	Cr	Cu
1-1-a	17	548	65	45	26	0	119	0	52
1-2-a	16	178	130	30	17	0	94	0	63
1-2-b	14	261	161	17	44	0	91	0	48
1-2-c	16	82	67	15	26	0	100	0	51
1-3-a	20	54	19	7	9	0	85	0	127
1-3-b	16	67	43	20	20	0	77	0	163
1-3-c	12	213	63	88	50	0	113	0	94
1-3-d	17	133	67	58	58	0	58	0	292
1-3-e	13	200	87	53	40	0	140	0	245
1-3-f	13	350	188	63	100	0	88	0	138
1-4-a	22	325	92	12	9	0	73	0	278
1-4-b	20	172	68	14	20	0	70	0	300
1-4-c	19	119	75	8	20	0	73	0	158
1-4-d	16	335	221	8	27	0	195	0	262
1-4-e	14	117	117	8	29	0	71	0	325
1-5-a	20	200	155	45	25	0	83	0	195
1-5-b	18	97	69	17	17	0	76	0	164
2-1-a	18	100	116	26	16	0	81	0	81
2-1-b	19	32	61	7	11	0	91	0	48
2-1-c	18	117	94	31	8	0	261	0	47
2-1-d	16	192	94	8	11	0	92	0	58
2-2-a	21	65	74	8	9	0	162	0	43
2-2-b	19	52	59	12	14	0	76	0	50
2-2-c	19	127	133	33	18	0	94	0	51
2-2-d	17	89	117	17	13	0	309	0	64

Table G1 (Continued)

Designation*	Carapace (mm)	Metal Concentration, μg/g							
		Fe	Mn	Ni	Pb	Cd	Zn	Cr	Cu
2-2-e	16	114	86	8	6	0	100	0	75
2-2-f	17	122	106	22	13	0	100	0	56
2-3-a	18	75	68	11	5	0	82	0	155
2-3-b	16	170	64	15	15	0	82	0	227
2-3-c	14	96	21	17	29	0	563	0	225
2-4-a	21	100	58	8	10	0	78	0	105
2-4-b	27	95	24	3	7	0	75	0	96
2-4-c	22	237	69	7	11	0	86	0	184
2-4-d	18	102	32	8	12	0	219	0	185
2-4-e	18	141	72	13	19	0	103	0	253
2-5-a	21	130	56	18	6	0	105	0	361
2-5-b	20	169	158	9	9	0	74	0	187
2-5-c	22	138	83	10	10	0	72	0	343
2-5-d	16	350	235	15	13	0	338	0	338
2-5-e	15	211	189	14	20	0	77	0	271
2-6-a	26	103	90	8	8	0	86	0	85
2-6-b	25	50	37	4	6	0	101	0	109
3-1-a	17	115	59	6	9	0	105	0	41
3-1-b	17	82	114	4	11	0	89	0	36
3-1-c	16	159	85	5	5	0	82	0	62
3-2-a	20	22	24	7	15	0	96	0	61
3-2-b	20	169	96	2	4	0	80	0	39
3-2-c	21	141	114	5	6	0	76	0	80
3-3-a	19	112	55	4	10	0	69	0	55
3-3-b	22	93	53	4	7	0	95	0	109
3-3-c	17	103	55	6	12	0	79	0	82
3-3-d	17	234	77	9	10	0	78	0	87

Table G1 (Continued)

Designation*	Carapace (mm)	Metal Concentration, μg/g							
		Fe	Mn	Ni	Pb	Cd	Zn	Cr	Cu
3-4-a	20	218	115	9	6	0	109	0	135
3-4-b	19	166	60	9	9	0	77	0	106
3-4-c	24	145	46	7	7	0	82	0	99
3-5-a	28	43	32	5	6	0	123	0	135
3-6-a	24	24	27	3	5	0	102	0	82
3-6-b	20	98	96	8	9	0	74	0	73
3-6-c	21	72	63	4	5	0	71	0	88
3-6-d	19	79	85	10	6	0	91	0	116
4-1-a	17	49	24	0	4	0	80	0	42
4-1-b	16	65	20	0	0	0	105	0	35
4-1-c	20	68	16	18	2	0	74	0	72
4-2-a	20	193	41	0	12	0	69	0	36
4-2-b	20	83	33	0	3	0	69	0	30
4-2-c	20	122	59	0	5	0	74	0	65
4-2-d	20	91	38	0	6	0	81	0	49
4-3-a	24	44	22	9	3	0	72	0	49
4-3-b	20	93	34	81	2	0	79	0	48
4-3-c	20	58	22	42	7	0	71	0	38
4-3-d	18	132	60	4	9	0	76	0	92
4-3-e	17	201	77	10	11	0	79	0	69
4-4-a	25	25	19	1	6	0	104	0	38
4-4-b	25	131	71	2	3	0	79	0	58
4-4-c	21	56	35	0	2	0	87	0	42
4-5-a	20	72	36	2	2	0	99	0	86
4-6-a	24	41	31	8	0	0	78	0	60
4-6-b	23	68	28	3	8	0	80	0	43
4-6-c	21	116	40	2	4	0	82	0	48
4-6-d	19	168	55	6	10	0	82	0	59

Table G1 (Continued)

Designation*	Carapace (mm)	Metal Concentration, μg/g							
		Fe	Mn	Ni	Pb	Cd	Zn	Cr	Cu
5-1-a	15	95	41	17	7	0	61	0	54
5-1-b	16	125	42	25	5	0	75	0	63
5-1-c	21	32	11	3	16	0	77	0	42
5-1-d	18	124	33	8	14	0	74	0	58
5-1-e	19	54	29	5	7	0	81	0	42
5-2-a	21	37	58	0	0	0	71	0	51
5-2-b	24	55	36	5	0	0	69	0	68
5-2-c	20	37	32	2	2	0	73	0	68
5-3-a	22	55	44	8	2	0	97	0	75
5-3-b	19	88	54	5	0	0	84	0	77
5-3-c	15	132	94	10	5	0	75	0	57
5-4-a	22	176	111	10	6	0	83	0	81
5-4-b	26	82	22	3	4	0	75	0	57
5-4-c	21	128	52	5	9	0	91	0	53
5-4-d	17	427	82	11	11	0	96	0	57
5-5-a	17	108	64	3	11	0	72	0	53
5-6-a	30	95	371	1	4	0	127	0	132

*First number refers to sampling date, second number refers to stream station, and the letter designates individual crayfish.

HEAVY METALS PARTITIONING IN A STREAM RECEIVING URBAN RUNOFF

by

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(ABSTRACT)

Water, sediment, detritus, caddisflies, snails, and crayfish were collected from Bull Run between July 31 and October 2, 1977 and analyzed for Fe, Mn, Ni, Pb, Cd, Zn, Cr, and Cu by atomic absorption spectrophotometry after appropriate digestion and extraction procedures. The samples were collected from six sampling stations along Bull Run which received sewage effluent, urban runoff, and stormwater drainage from the Manassas area. Sampling stations included an upstream control located well above the urban area, four stations located immediately above and below suspected stormwater inputs, and a station sufficiently removed from direct stormwater input.

Concentrations of Pb and Cu in water, sediment, detritus, and caddisflies increased with increasing distance downstream and were significantly (0.95 level) greater in these components immediately below the stormwater input than at the upstream control. Concentrations of Pb in sediment collected at a downstream station were significantly greater than those at the control station even though the control sediment characteristics favored metal retention more than the downstream sediment characteristics. Mean Cu concentrations in sediments at this station

were greater (but not significantly) than at the upstream control station while all other metals were concentrated the least in sediment at the downstream station. Significant (0.95 and 0.99 level) linear correlation coefficients among a majority of stream components were found for Pb and Cu. It appears that urban runoff and stormwater drainage contributed sufficient quantities of Pb and Cu into Bull Run such that these metals accumulated greater in stream components below the Manassas urban area.