EFFECTS OF HIGH DISCHARGE AND AN OIL REFINERY CLEANUP OPERATION ON HEAVY METALS IN WATER AND SEDIMENTS IN SKELETON CREEK*

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Distribution of copper, chromium, lead, and zinc in water and sediments was studied in Skeleton Creek, Oklahoma, following conditions of high discharge and after an oil refinery cleanup operation. Heavy metal concentrations in water generally decreased exponentially with time following high stream discharge while no significant trends existed in the distribution of heavy metals in sediments. Copper concentration in water generally decreased with time while chromium, lead, and zinc exhibited peak concentrations 4 to 8 days after the date effluents from an oil refinery cleanup were expected to enter Skeleton Creek. No significant changes in metal concentrations occurred in the sediments.

INTRODUCTION

Considerable variation exists in the distribution of metals in freshwater ecosystems. Heavy metals generally exist in low levels in water and attain considerable concentration in sediments and biota (1, 2). Metals accumulated in stream sediments are removed from upstream areas during high discharge and deposited farther downstream (3, 4). It is not known if metal concentrations of stream sediments undergo net change following heavy rainfalls and a period of high stream discharge and scouring.

Municipal and industrial discharges and surface water runoff add significant amounts of trace metals to sediments of aquatic ecosystems (5, 6). Heavy metals present in crude oils or added during the refining process accumulate on the refinery equipment (7). Refinery equipment is cleaned annually during the summer, and it is expected that this leads to a change in metal content of the oil refinery effluent. The objectives of this study were to (a) measure the concentrations of copper, chromium, lead, and zinc in water and sediments in Skeleton Creek, Oklahoma, (b) determine the effect of high discharge on concentrations of metals in water and sediments, and (c) determine if oil refinery equipment cleaning increases the concentrations of metals in water and sediments.

DESCRIPTION OF SKELETON CREEK

Skeleton Creek originates near Enid, Garfield County, Oklahoma, flows southeasterly for 113 km through Kingfisher and Logan Counties, and empties into the Cimarron River 8 km north of Guthrie. Skeleton Creek passes from a third-order stream at the upstream station to a sixth-order stream at the downstream station (8). The watershed area is approximately 106,230 ha.

Municipal and industrial wastes enter the headwaters of Skeleton Creek from five sources. Effluents from an aerated domestic sewage lagoon in North Enid and from the Enid State School sewage treatment plant enter the creek directly. Other wastes enter Skeleton Creek in the discharge of Boggy Creek, a stream which originates southwest of Enid. These wastes include the effluents from the domestic waste treatment plant at Vance Air Force Base, from oxidation ponds of the Champlin Oil Refinery, and from the Enid municipal sewage treatment plant.

METHODS

Grab samples of water and sediment were collected between 4 Apr and 25 Oct 1973. Two stations were selected and numbered according to their distance in kilometers (6 and 97) from the confluence of Boggy Creek with Skeleton Creek. Samples were collected at six different times two days after a f1ood subsided, and thrice, twice, and once 4, 8, and 16 days, respectively, after a flood subsided. Sediment samples

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Proc. Okla. Acad. Sci. 56: 133-138 (1976)

were collected at Station 6 and 97 on October 19 and 25 after the Enid area received 40 cm of rainfall in 24 hr. Collections for comparisons before and after refinery cleanup were made 1 day before and 2, 4, 8, and 16 days following the date effluents from the refinery were expected to reach Skeleton Creek.

Five water samples and six sediment samples were collected from the stations on each sampling date. Water samples were collected in 250-ml plastic bottles at one-half the total water depth; sediment samples were cores 3 cm in diameter and 5 cm long. Water samples were preserved with nitric acid and sediment samples were frozen until metal analyses were made. Concentrations of the four metals in water samples were determined with a graphite furnace atomic absorption spectrophotometer. Approximately 15 g of the top 5 cm of sediment from each core was extracted with 1*N* nitric acid. Heavy metal concentrations of the extracts were determined by aspirating the liquid into a flame atomic absorption spectrophotometer; results are expressed as μg/g dry sediment weight.

Approximately 10 g dry weight sediment from each core was ignited at 500 C for 12 hr to obtain loss on ignition as an estimate of organic matter content. Daily precipitation data were obtained from Radio Station KCRC, Enid, Oklahoma. Mean daily discharge was gauged at kilometer 76 by the U.S. Geological Survey (9).

RESULTS

Conditions Following High Discharge

Frequent rains during April, May, and June caused large fluctuations in daily stream discharge. Such discharge increased considerably after precipitation in April and May, but much less in June because of less runoff owing to reduction in soil moisture (Figures 1 and 2).

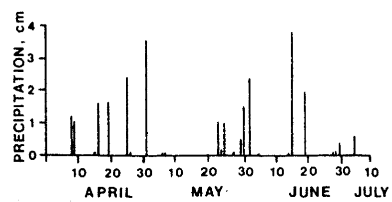

FIGURE 1. Daily precipitation recorded at Enid, Oklahoma.

Combined copper concentrations of specific days after a rainfall for the various sets of samples decreased significantly with time ($p = 0.02$) (Table 1). Linear regression analysis showed that the variation of copper reduction with time approached a logarithmic curve:

log Y = 0.6407 – 0.0222 X, where Y = the copper concentration and X = days following high flow.

The regression coefficient was significantly different from zero ($0.001 < p < 0.01$), indicating that copper was reduced rapidly the first few days following high flow.

Concentration of chromium in Skeleton Creek decreased significantly ($p = 0.08$) with time after a rainfall (Table 1). The following linear regression of decrease in chromium with days after high discharge approached a logarithmic curve:

log Y = 0.4593 – 0.0188 X

The coefficient was significantly different

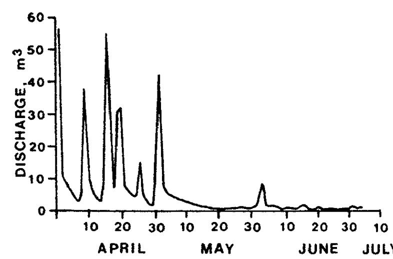

FIGURE 2. Mean daily discharge recorded at Kilometer 76.

TABLE 1. *Metal concentrations in water and turbidity for each day following high stream discharge adjusted by multiple regression analysis for differences between stations and among sampling sets.*

Number of days following high discharges	Concentration (μg/l)			Turbidity (JTμ)
	Copper	Chromium	Zinc	
2	3.8	3.2	10.2	173
4	3.8	2.2	4.3	92
8	2.8	1.6	2.4	75
16	1.9	1.6	2.3	120

from zero at the 0.08 level.

A large reduction in zinc concentration occurred in Skeleton Creek during the first 8 days following the high stream discharge (Table 1). However, differences among the means for days after high flow were not significant because of large variation in zinc concentrations between the two sampling stations and among the different sampling dates. The following linear regression was used to see if the observed means fit a logarithmic equation:

$$\log Y = 0.8957 - 0.0396\, X$$

The regression coefficient was different from zero at the 0.08 level.

Heavy metals in Skeleton Creek sediments showed little variation in mean concentrations when values for specific days following high stream discharge of the various sets of samples were combined (Table 2). Mean levels of copper and lead increased slightly with time after high flow. No trend was evident for chromium and zinc concentrations. Differences among means for each heavy metal for days after high stream discharge were not significant. Loss on ignition did not increase with time after high flow in Skeleton Creek sediments.

Heavy metals in sediments were found in higher concentrations after one of the worst floods in the history of Skeleton Creek. On 10 Oct 1973, a rainfall of 39.83 cm in 24 hr resulted in a peak discharge on 12 Oct of 444.62 m^3/sec at Kilometer 76. Means of the sediment cores collected on 19 and 24 Oct at Station 6 and 97 are presented in Table 3. Sediment samples had higher heavy metal concentrations on 19 Oct than on 24 Oct at Station 6. However, differences between day means were not significant because of the high variation among the six cores on each date. In contrast, the Station 97 mean was significantly higher on 24 Oct than on 19 Oct. Copper increased by 1.43 μg/g ($0.01 < p < 0.02$), chromium by 2.40 μg/g ($0.02 < p < 0.05$), lead by 2.18 μg/g ($p = 0.08$), and zinc increased by 4.46 g/g ($p = 0.08$) from 19 to 25 Oct.

Higher heavy metal concentrations in sediments in October were believed to be due to scouring of oil refinery holding ponds during flooding and the deposition of suspended matter carrying the metals in Skeleton Creek sediments. Large patches of oily material were found along the shore and in the sediments on the October sampling dates. Two cores from Station 6 on each sampling date had black oily residues included. Concentrations of copper, chromium, lead, and zinc and percent loss on ignition were much higher in these cores (Table 4).

TABLE 2. *Metal concentrations in sediments for each day following high stream discharge adjusted by multiple regression analysis for differences between stations and among sampling sets.*

Number of days following high discharge	Concentration (μg/g)				Loss on ignition (%)
	Copper	Chromium	Lead	Zinc	
2	1.9	6.1	3.2	12.9	2.2
4	1.9	5.8	3.5	13.7	2.3
8	2.0	6.7	3.6	11.8	2.1
16	2.2	5.2	4.9	13.6	1.8

TABLE 3. *Means and standard deviations of copper, chromium, lead, and zinc after October flood,* 1973.

Dates	Station	Concentration (μg/g)			
		Cu	Cr	Pb	Zn
19 Oct 73	6	5.45	10.03	11.21	27.17
		(6.41)[a]	(8.01)	(13.54)	(32.94)
	97	1.41	5.14	3.93	5.40
		(0.48)	(1.26)	(1.34)	(1.86)
25 Oct 73	6	3.90	6.71	9.08	16.22
		(4.45)	(3.55)	(8.63)	(12.85)
	97	2.84	7.54	6.11	9.86
		(1.02)	(2.13)	(2.20)	(5.04)

[a]Standard deviations are in parentheses.

Conditions Following Refinery Cleanup

Environmental conditions in Skeleton Creek following refinery cleanup procedures were influenced by a total precipitation of 4.22 cm on 23, 24, 25, 28, 30, 31 May and 2 June. Oil refinery effluents from the cleanup were expected to reach Skeleton Creek on 27 May (Mr. Bruce Hodgden, Champlin Oil Refinery, Enid, Oklahoma).

Copper concentration at Skeleton Creek Station 6 decreased with time during the study and decreased after 29 May (Day 2) at Station 97 (Table 5). Differences among means of sampling dates were highly significant ($p < 0.0005$); however, the results are complicated by increased runoff and discharge in Skeleton Creek during the study period.

Highest chromium concentrations occurred on Day 4 at Station 6 and on Day 8 at Station 97 (Table 5). Lowest means occurred on Day 2 at both stations. Variation among sampling dates was highly significant ($p < 0.0005$).

Lead in Skeleton Creek water averaged 24.0 μg/l on Day 4 at Station 6 and 12.2 μg/l on Day 8 at Station 97 (Table 5). Because these were the only two means above detectable levels in the statistical analysis, differences among sampling dates were highly significant ($p < 0.0005$).

Zinc concentration was highest on Day 4 at Station 6 and on Day 8 at Station 97 (Table 5). As for chromium and lead, variation of means among sampling dates was highly significant ($p < 0.0005$).

Regular changes in heavy metal concentrations similar to those found in water did not occur in the sediments of Skeleton Creek following oil refinery cleanup or

TABLE 4. *Mean values for cores containing oily materials.*

Dates	Core	Concentration (μg/g) Cu	Cr	Pb	Zn	Loss on ignition (%)
19 Oct 73	1	9.06	10.36	16.23	29.78	3.85
	2	16.99	6.48	36.70	92.29	2.80
24 Oct 73	1	7.21	9.01	14.29	26.72	4.60
	2	11.37	10.66	23.68	36.11	3.05

TABLE 5. *Metal concentrations in water for sampling dates following refinery cleanup.*

Number of days following refinery cleanup	Station	Concentration (μg/l) Copper	Chromium	Lead	Zinc
−1	6	9.2	8.0	N.D.[a]	13.8
	97	5.8	4.6	N.D.	13.6
2	6	2.6	N.D.	N.D.	6.4
	97	6.2	1.0	N.D.	2.0
4	6	2.4	3.8	24.0	35.6
	97	3.8	4.0	N.D.	5.4
8	6	2.4	1.6	N.D.	3.6
	97	3.0	4.8	12.2	25.8
16	6	1.2	0.6	N.D.	1.6
	97	N.D.	1.8	N.D.	0.2

[a]N.D. — not detected.

TABLE 6. *Metal concentrations in sediments for sampling dates following refinery cleanup.*

Number of days following refinery cleanup	Station	Concentration (μg/g) Copper	Chromium	Lead	Zinc
−1	6	2.3	9.6	5.3	22.3
	97	2.2	6.9	3.8	11.9
2	6	1.6	7.1	2.7	18.2
	97	2.7	6.9	4.2	13.6
4	6	2.0	7.0	4.1	19.3
	97	2.5	6.7	3.8	12.4
8	6	1.5	5.6	3.0	17.9
	97	2.3	5.1	4.0	12.2
16	6	2.3	7.4	4.2	18.3
	97	2.3	7.2	4.3	11.8

following increased stream discharge from runoff in early June (Table 6). No significant differences existed in heavy metal concentrations among the five means for days after high flow.

DISCUSSION

Conditions Following High Discharge

Correlations between heavy metal concentrations and stream flow are not consistent for various studies. Measurements of heavy metals during low and high flow conditions showed that metals were positively correlated with discharge in one river and often were negatively correlated in another river (10). Although copper in suspended particulates coincided with high stream flow, other metals did not show this behavior in streams of the Cayuga Lake Basin, New York (11). Andelman (12) concluded in a review article that no systematic correlation existed between metal concentrations and stream flow. Heavy metal concentrations increased rapidly with increased discharge and turbulence and quickly decreased following high stream discharge in the Ohio River, Ohio, and Black Warrior River, Alabama (3, 4). Skeleton Creek data correspond to the trend of decreased metals with time after high flow. Zinc concentration in the Ohio River at Cincinnati increased from 2 μg/l to over 19 μg/l and then decreased to less than 1 μg/l in 15 days during rapid changes in stream discharge. These fluctuations were attributed to resuspension of bottom particles during the increased turbulence. A positive correlation also existed between resuspended bottom sediments and heavy metal concentrations in the total water column of the Black Warrior River. However, no increase occurred in the metal levels in solution. The largest resuspension of bottom sediments occurred during high discharge and scouring from heavy rain runoff. A similar condition occurred in Skeleton Creek because metal levels and turbidity generally decreased with time after high flow.

Minor fluctuations in the heavy metal content of Skeleton Creek sediments may be attributed to localized redistribution of sediments. Stream sediments are scoured and resuspended at higher discharge (13). Heavy metals were associated with particulate material in the Ohio and Black Warrior Rivers, and metals were found in greater concentrations in suspended materials during high discharge (3, 4). Few investigators have reported changes in metal concentrations in stream sediments following high discharge. The processes of scouring and filling occur simultaneously in streams with a net loss of sediment downstream (13). Ohio and Black Warrior River sediments accumulated organic material and heavy metals with time coinciding with low stream flow and sediment accumulation (3, 4). Organic material did not increase with time following high flow in Skeleton Creek sediments.

Conditions Following Refinery Cleanup

Slug loads of chromium, lead, and zinc entered Skeleton Creek on approximately May 31 (Day 4). High concentrations of these metals were found 4 days later at Station 97. The date that effluents from oil refinery cleanup processes were expected to reach Skeleton Creek was estimated by approximate time needed for wastes to pass through the water treatment facilities. The Day 0 estimate may have been in error and the actual date of discharge into Skeleton Creek may have been May 31 (Day 4). The source of these heavy metals could not be identified solely as oil refinery wastes since runoff from Enid also may have affected the metal content of the water. High heavy metal concentrations ranked in decreasing order of abundance in street runoff were lead, zinc, chromium, and copper, respectively (14, 15). Street surfaces which had been flushed by a recent rain had lower metal concentrations in the runoff than runoff from streets without a recent flushing (14). Enid streets had been flushed on three occasions a few days prior to the May 31 (Day 4) samples. Thus, slug loads of heavy metals observed in Skeleton Creek were not expected from runoff alone.

Higher levels of heavy metals in Skeleton Creek water were not reflected by higher levels in the sediments possibly because the increased flow reduced the amount of metals that became associated with sediments. This probably occurred because metals were associated with the fine suspended particles which were not deposited on the stream bed during high discharge conditions.

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