

# THE DISTRIBUTION OF COPPER, LEAD, AND ZINC IN THE SEDIMENT AND WATER OF LAKE CARL BLACKWELL

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Concentrations of copper, lead, and zinc in Lake Carl Blackwell were far below the maximum levels permitted in domestic water supplies by the United States Public Health Service. Although no statistical difference was found in metal content of the water between deep water and shallow water areas of the lake, significant differences were observed between metal content of surface water and bottom water and in temporal variation of the metals in water. Highest concentrations occurred after a period of rainfall, suggesting that runoff contributed to the metal content of the water. The concentration of metals in sediments of deep water stations was significantly greater than shallow water stations. Metal concentrations in shallow water sediments generally decreased with increasing sediment depth. In contrast, metal content of deep water sediments was relatively uniform over depth. The variation between deep and shallow water stations and the variation with depth in shallow water stations may be influenced by wind-driven currents and particle size.

Heavy metals have been accumulating for years in sediments, water, and biota of lakes and streams. Lucas et al. (1) stated that "trace contaminants may have effects on the ecosystem as great or greater than those of the more common pollutants." Six heavy metals have been found frequently in the aquatic areas of this region (personal communication, Gordon Wallace), while four, viz., copper, chromium, lead, and zinc, have been classified as having a "very high pollution potential" (2).

Heavy metals and salts of heavy metals are found in many agricultural runoffs and industrial wastes. Lake Carl Blackwell, a man-made impoundment, receives runoff primarily from natural and agricultural sources. No information is available about the metal content of the lake. The objectives of this study were to (a) compare the concentration of three heavy metals in the sediment and water of deep, relatively undisturbed areas of Lake Carl Blackwell with shallow areas having well circulated water, (b) observe if heavy metal concentration is changed following precipitation, and (c) determine vertical distribution of heavy metals in the sediment and water.

Lake Carl Blackwell, located in Payne County, 11 km west of Stillwater, Oklahoma (3), serves as the water supply for the city of Stillwater. Although the surface area is 1500 ha at spillway elevation, the lake was 5.4 m below spillway level during the study. The main body of the reservoir is oriented

in an east-west direction and at right angles to prevailing southerly winds. Because of the shallowness of the lake and the low, unprotected surrounding areas, wind induced currents keep the lake water circulated and turbid. The reservoir's flood plain is relatively level with few irregularities except the former stream channel which lies 1-3 m below the plain. The drainage basin, part of the Cimarron River Basin, is 172 km<sup>2</sup> in area, and soils of the region were derived from red Permian clays and shale. The majority of the land surrounding the reservoir is used for grazing although a small amount of wheat and sorghum farming is conducted.

## METHODS

### Field Methods

Sediment and water samples were collected on 9, 14, 26, and 30 September and 7 October, 1972. Two sediment samples were obtained at each of seven stations. Water depth at the four shallow water stations ranged from 1.5 to 2.5 m and the bottom was well circulated by wind induced currents. Water depth at the three deep water stations varied from 4.0 to 8.5 m and the bottom was relatively undisturbed.

Sediment samples were taken with a vertical core sampler (G.M. Manufacturing & Instrument Co.), equipped with a 3 x 60 cm polyethylene insert. After collecting the sample, inserts were frozen until analyses

were made. Water samples were taken at each station from the surface and from the bottom with a Van Dorn water bottle. A 250 ml sample was withdrawn, placed in a polyethylene bottle, and acidified with 2 ml of concentrated nitric acid. The pH of the water was thus kept below 2 to prevent altering the metal content of the sample.

#### Laboratory Methods

Each frozen sediment core was cut into as many of the following layers as its length would permit: 0-1, 2-3, 4-5, 9-10, 14-15, 19-20, 29-30, 39-40, and 49-50 cm (4, 5, 6). Approximately 5g of each layer were placed in a tared 200 ml polyethylene flask. The sediment sample was dried in an oven for 12 h at 105 C, placed in a desiccator for 1 h, and then reweighed. Fifty ml of 1 N nitric acid were added to each flask. The flasks were shaken for 12 h on an Eberbach shaker (7, 8, 9) and then left undisturbed for 24 h to permit sedimentation. The liquid was aspirated into a Varian Techtron flame atomic absorption spectrophotometer and analyzed for the presence of copper, lead, and zinc. Absorbance values recorded from the spectrophotometer were compared to a curve of standard concentrations for calculation of the metal content of the liquid. A hydrogen continuum spectrum lamp was used to correct for background interference. Final calculation of metal content of the sediment was done using the equation,

$$\frac{\text{metal in solution (mg/l)}}{\text{metal in sediment } (\mu\text{g/g})} \times \frac{50 \text{ ml}}{\text{sample wt (g)}} =$$

Water samples were analyzed for metal content with a Perkin-Elmer heated graphite atomizer (HGA-70) attachment to the atomic absorption spectrophotometer. A 20  $\mu$ l sample was pipetted into the carbon rod of the graphite atomizer. During atomization of the sample, the resultant absorbance peak was recorded on a Beckman recorder. If contamination of the pipette was suspected and an unusually high peak recorded, the injections were repeated until two peaks of the same height were observed. Corrections for background interference were made with a hydrogen continuum spectrum lamp. Final calculations of metal concentrations were made by comparing the recorded

peak heights to a curve of standard concentrations.

Comparison of metal concentration in the water and sediment over the five time periods at seven stations were done by analysis of variance. Variation between metal concentration in the surface water and the water-sediment interface and variation with depth for the sediment cores were also determined by analysis of variance.

## RESULTS

### Copper, Lead, and Zinc in Water

Since no significant difference existed in metal concentration in the water among stations or between the combined shallow water and the combined deep water areas in Lake Carl Blackwell, these data were combined in Table 1. Copper concentration

TABLE 1. Range and mean concentrations of heavy metals measured in surface and bottom waters collected from seven stations at five time periods in Lake Carl Blackwell, Oklahoma.

Site	Copper ( $\mu\text{g/l}$ )		Lead ( $\mu\text{g/l}$ )		Zinc ( $\mu\text{g/l}$ )	
	Range	$\bar{x}$	Range	$\bar{x}$	Range	$\bar{x}$
Surface	2-13	4	1-3	2	2-42	10
Bottom	3-17	6	2-8	3	5-97	28

varied from 2 to 17 $\mu\text{g/l}$  and averaged 5. Copper content of the water at the surface was significantly less than at the bottom. ( $p=0.01$ ). Temporal variation in copper content of the water also was statistically significant ( $p = 0.05$ ). Highest overall mean concentrations were on 9 September and 14 September. Lake Carl Blackwell received 3.40 cm of rain on 8 and 9 September which suggests that runoff may have contributed to the copper content of the water. Low mean concentrations of 4  $\mu\text{g/l}$  occurred on 26 and 30 September after periods of low rainfall.

The concentration of lead varied from 1 to 8 $\mu\text{g/l}$  (Table 1) and averaged 3. The variation between lead content of the water at the surface and bottom was small, but statistically significant ( $p = 0.05$ ). Temporal variation in lead content of water was statistically significant. The mean concentrations on 9 September and 14 September were higher than the mean concentrations of other days.

Zinc concentration was considerably higher than the concentration of copper or

lead. Values ranged from 2 to 97  $\mu\text{g}/\text{l}$  and averaged 19 (Table 1). Mean concentration of the surface water, 10  $\mu\text{g}/\text{l}$ , was significantly lower than the mean concentration of the interface water, 28  $\mu\text{g}/\text{l}$ . Temporal variation in the zinc concentrations of the water was significant. The highest means, 35  $\mu\text{g}/\text{l}$  on 9 September and 29  $\mu\text{g}/\text{l}$  on 14 September, were greater than the means of other days. The lowest mean concentration was 8  $\mu\text{g}/\text{l}$  on 26 September.

#### Copper, Lead, and Zinc in Sediment

Although considerable variation existed among stations and over time in heavy metals in the sediments of Lake Carl Blackwell, no consistent trend was apparent and data from the shallow water stations and the deep water stations were combined in Table 2. The mean concentration of copper

TABLE 2. Range and mean concentrations of heavy metals in shallow and deep water sediments collected in cores at five time periods.

Depth (m)	Copper ( $\mu\text{g}/\text{g}$ )		Lead ( $\mu\text{g}/\text{g}$ )		Zinc ( $\mu\text{g}/\text{g}$ )	
	Range	$\bar{x}$	Range	$\bar{x}$	Range	$\bar{x}$
1.5-2.5	4.4-13.9	10.1	5.4-13.9	19.5	13.4-48.9	34.1
4.9-8.5	4.4-17.6	12.9	5.3-48.9	30.7	10.9-76.9	48.5

in shallow water stations, 10.1  $\mu\text{g}/\text{g}$ , was significantly different ( $p = 0.01$ ) from deep water stations, 12.9  $\mu\text{g}/\text{g}$ . The maximum mean concentration was measured on 14 September, 5 days after the area received 2.79 cm of rain which indicates that runoff may have contributed to the increased copper content of the sediments. Copper concentration decreased with depth at the shallow water stations from 10.9  $\mu\text{g}/\text{g}$  at 0-1 cm to 4.4  $\mu\text{g}/\text{g}$  at 39-40 cm. The concentration was relatively uniform with depth at the deep water stations.

Lead content in sediments varied from 5.3 to 48.9  $\mu\text{g}/\text{g}$  and averaged 38.4 (Table 2). The means of 19.5  $\mu\text{g}/\text{g}$  for the shallow water stations and 30.7  $\mu\text{g}/\text{g}$  for the deep water stations were statistically different ( $p = 0.01$ ). The maximum concentration of lead was measured 5 days after the area received a heavy rain, as was observed for copper. Lead decreased with depth at the shallow water stations from 26.7  $\mu\text{g}/\text{g}$  at 4-5 cm to 4.6  $\mu\text{g}/\text{g}$  in the 39-40 cm layer. Little variation existed among concentrations at the various depths in the deep water stations.

Concentration of zinc varied from 10.9 to 48.9  $\mu\text{g}/\text{g}$  and averaged 41.3 (Table 2). The means of the deep water stations, 48.5  $\mu\text{g}/\text{g}$ , and shallow water stations, 34.1  $\mu\text{g}/\text{g}$ , were statistically different at the 0.01 level. Temporal variation in zinc ranged from 34.4  $\mu\text{g}/\text{g}$  on 9 September to 43.7  $\mu\text{g}/\text{g}$  on 14 September. As with copper and lead, zinc decreased with depth at the shallow water stations and was relatively uniform at deep water stations. Values at the shallow water stations decreased from 38.5  $\mu\text{g}/\text{g}$  at 4.5 cm to 18.4  $\mu\text{g}/\text{g}$  in the 39-40 cm layer.

#### DISCUSSION

Concentrations of heavy metals in Lake Carl Blackwell water were below or within the range of concentrations found in other locations (10-15). The mean values of 5, 3, and 19  $\mu\text{g}/\text{l}$  for copper, lead, and zinc are considerably less than the maximum allowed standards of 100, 50, and 5000  $\mu\text{g}/\text{l}$ , respectively, specified for drinking water by the United States Public Health Service (16). The concentrations observed in the water of Lake Carl Blackwell were well below levels reported to be toxic. The 96-hour TLM for a freshwater snail (*Pbyssa heterostrophha*) was 790 to 1270  $\mu\text{g}/\text{l}$  zinc (17). A copper concentration of 1250  $\mu\text{g}/\text{l}$  was reported as the 96-hour TLM for the bluegill (*Lempomis macrochirus*) (18).

The mean content of copper, lead, and zinc in the sediments of Lake Carl Blackwell was 11.5, 38.4, and 41.3  $\mu\text{g}/\text{g}$ , respectively. Those values are below or within the range of values reported in the literature (6, 19-23). Although results are variable, a tendency exists for heavy metals to decrease with sediment depth (4, 6, 21, 24). The concentrations of all three metals were higher in the sediments of deep water stations of Lake Carl Blackwell than in shallow water sediments. Metal concentrations at deep water stations were relatively uniform over sediment depth, while at shallow water stations concentrations decreased with sediment depth. The sediment was frequently resuspended by wind-driven wave action in shallow water areas. As the sediment was redeposited, the larger sand and silt particles were deposited first. Because of the larger surface area/volume ratio associated with clay particles, a greater area exists to which heavy metal ions can adhere. Thus, more heavy metals were deposited in

the upper layers of sediment with clay particles than in the deeper layers with sand and silt particles. This also may explain why deep water stations had higher but more uniform concentrations of copper, lead, and zinc. Larger quantities of clay particles were transported into deep water, thus carrying with them more heavy metal ions. Sand and silt particles, however, were deposited in shallow water. The clay particles, once deposited, were undisturbed because of the depth of the water.

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