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THE concentrations of zinc found in natural waters are very low. Observed zinc levels are well below those limits set by the solubilities of zinc carbonate and zinc hydroxide. An idea of the range of zinc concentrations encountered may be obtained from a brief review of the literature.

Previous Research

In an extensive program of sampling and analysis of Columbia River water,[1] USPHS recorded a maximum of 130 and a minimum of 10 ppb zinc. Only four of the 34 samples analyzed showed the presence of more than 50 ppb zinc. The Columbia River consistently exhibits a pH close to 8.0.

Studies by Carritt and Renn [2] on the James River in Virginia indicated a maximum of 96 ppb and a minimum of 8 ppb zinc—the latter the limit of detection with a polarographic technique. Samples were taken at points downstream from industrial discharges of zinc-bearing wastes. Only two of the sixteen samples analyzed showed the presence of more than 50 ppb zinc. The average pH was 7.4.

Heide and Singer [3] reported zinc levels of 116–332 ppb in the Saale River, which flows through a highly industrial region in Germany and which receives, at one point, wastes containing 3,500 ppb zinc. One kilometer below the point of discharge the river silt contained 0.88 per cent zinc. These investigators demonstrated, as did Carritt and Renn, that the zinc is lost from solution shortly after being discharged into the stream.

Kehoe, Cholak, and Sargent [4] have compiled data on zinc and other trace metals in drinking waters in 37 locations in the United States. The mean of the concentrations recorded is 136 ppb. This work is of particular interest both because of its geographic extent and the variety of drinking water sources tested. No relationship between source and zinc content was found, however, as lake, river, and well waters may be either relatively high or relatively low in zinc content.

Huff [5] describes zinc concentrations in water in Colorado and Missouri. Most values compared well with those values given by previous researchers; however, the levels of 98 and 60 ppm were reported in mine drainage, where the pH was 3.0. Streams draining mining districts showed an average of

530 ppb zinc, whereas the streams draining few or no mines showed 13 ppb zinc. It is interesting to note that the author sought to predict the location of mineral deposits through trace metal analysis.

On the basis of this previous work, therefore, it may be concluded that zinc concentrations found in natural waters free from mine drainage and industrial wastes may range from 10 to 200 ppb.

Present Study

Samples of stream water were collected from 33 stream sampling points on twenty streams in the Chesapeake Bay region for zinc analysis. At some locations, samples were taken of muds and silts from the surface of the river bed in an accessible backwater. Table 1 gives the location of sampling sites, date of sampling, zinc content of the water, pH, alkalinity, total hardness, and calcium hardness for water in the Chesapeake Bay region. Table 2 shows results of analyses performed on water collected from streams in the southeastern United States. Table 3 gives the zinc concentration of the bottom solids collected. All values were derived by the dithizone compleximetric method of Sandell.[6]

For convenience, the Chesapeake Bay sampling region is divided into the four subregions—that north of Baltimore, Maryland's eastern shore, the Potomac River Basin, and the region south of Baltimore.

Region North of Baltimore

The Gunpowder Falls and Susquehanna rivers are sources of municipal water supply for Baltimore and are located north of the city. Gunpowder Falls water is low in alkalinity and hardness, has near-neutral to slightly alkaline pH, and is relatively free from pollution of any type.

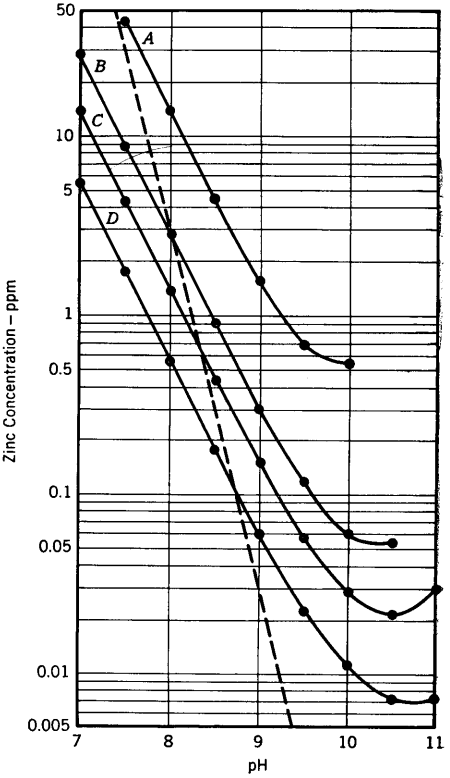

Fig. 1. Solubility of Zinc in Distilled Water as a Function of pH and Alkalinity

The dashed curve is for the solubility of zinc as zinc hydroxide; the solid curves, as zinc carbonate. Curve A *is for 10 ppm alkalinity;* B, *50 ppm;* C, *100 ppm; and* D, *250 ppm.*

The Susquehanna River, on the other hand, receives industrial and municipal waste discharges and mine drainage. The river is slightly acid and low in hardness-producing cations and alkalinity.

The highest concentrations of zinc found in the Chesapeake Bay region were found in these two streams. The Susquehanna River receives zinc-

TABLE 1

Analysis of River Waters in the Chesapeake Bay Region

Location of Sample Station	Date of Sampling	Zinc (Zn^{++}) Concn. *ppb*	pH	Total Alkalinity (as $CaCO_3$) *ppm*	Total Hardness (as $CaCO_3$) *ppm*	Calcium Hardness (as $CaCO_3$) *ppm*	Suspended Solids Concn. of Unfiltered Sample *ppm*
Region North of Baltimore							
Big Gunpowder Falls R.	3/9/60*	116	7.8	44	72	40	
Perry Hall, Md.		115					
Loch Raven Reservoir	7/8/61	63	9.0				
Prettyboy Reservoir	7/8/61	34	7.2				
Jones Falls	7/8/61	15	7.7				68
Butler, Md.							
Above Rockland Bleach & Dye Co.	7/8/61	24	7.4				41
Baltimore, Md.							
Susquehanna River	3/9/60	84	7.7	30	84	52	
Columbia, Pa.							
Millersburg, Pa.	9/27/60*	44	7.8				
		34					
Eastern Channel, 2.5 mi below	9/27/60	45	7.1				
Danville, Pa.							
East Shore	9/27/60	155	5.6				
Danville, Pa.							
West Channel	9/27/60	120	5.9				
Danville, Pa.							
Region of Maryland's Eastern Shore							
Choptank River	4/3/60	73	6.7	12	28	20	
Denton, Md.							
Nanticoke River	4/3/60*	87	6.9	10	20	16	
Seaford, Del.		90					
Vienna, Md.	4/3/60*	89	6.7	7	32	20	
		86					
Pocomoke River	4/3/60*	60	6.5	6	24	12	
Pocomoke City, Md.		55					
Tuckahoe River	4/3/60	95	7.2				
Hillsboro, Md.							
Wicomico River	4/3/60	61	6.9	14	24	16	
Salisbury, Md.							
Region of Potomac River Basin							
Monocacy River	3/13/60*	85	7.7	56	88	64	
Frederick, Md.		81					
	5/23/61	280	8.1				1,860
		13					
	5/23/61	13	8.0				4
		20†					
Potomac River	3/13/60	51	7.9	80	120	80	
Harper's Ferry, W. Va.							
	5/23/61	31	8.2				14
		32†					
Point of Rocks, Md.	3/13/60	65	7.8	40	64	44	
Shenandoah River	3/13/60*	61	8.1	114	140	88	
Harper's Ferry, W. Va.		61					
	5/23/61	27	8.1				9
		18†					
	5/23/61	580	8.3				2,560
		12†					

* Two samples. † Filtered sample.

TABLE 1—*Analysis of River Waters (contd.)*

Location of Sample Station	Date of Sampling	Zinc (Zn^{++}) Concn. *ppb*	pH	Total Alkalinity (as $CaCO_3$) *ppm*	Total Hardness (as $CaCO_3$) *ppm*	Calcium Hardness (as $CaCO_3$) *ppm*	Suspended Solids Concn. of Unfiltered Sample *ppm*
Region of Potomac River Basin (contd.)							
Shenandoah River (cont.)							
North Branch Front Royal, Va.	9/15/60	25	8.1	133	168	84	
	9/28/60	30	8.2				
	5/23/61	38	8.1				1,450
		32†					
	5/23/61	31	8.3				11
		29†					
South Branch, above Front Royal, Va.	4/11/60	92	7.8	71	96	68	
South Branch Front Royal, Va.	9/15/60*	20	7.9	139	164	96	
		21					
	9/28/60	19	8.3				
South Branch, above Front Royal, Va.	5/23/61	38	8.2				349
		12†					
	5/23/61	23	8.1				8
		14†					
South Branch Elkton, Va.	9/15/60	27	8.0	137	160	96	
South Branch, 2.5 mi south of Elkton, Va.	5/23/61	17	8.2				28
		20†					
	5/23/61	21	8.0				19
		18†					
Region South of Baltimore							
Appomattox River Macon, Va.	4/17/60‡	94	7.2	26	32	20	
		98					
		95					
James River Goochland, Va.	4/17/60	55	7.6	37	52	36	
Mattaponi River Aylett, Va.	4/17/60	44	6.6	7	16	8	
Pamunkey River Old Church, Va.	4/17/60‡	95	7.3	14	20	12	
		87					
		87					
Patuxent River Bowie, Md.	4/17/60*	60	7.0	14	28	20	
		56					
Upper Marlboro, Md.	6/28/61	20	7.7				76
Liberty Dam (face), Md.	7/9/61	29	7.6				13
Liberty Dam (backwater)	7/9/61	15	7.3				41
Rappahannock River Fredericksburg, Va.	4/17/60	61	7.2	16	49	16	
	5/10/61	24	7.6				6
		21†					
	5/10/61	26	7.6				8
		15†					
	5/10/61	24	7.6				7
		21†					
Port Royal, Va.	4/17/60	87	6.6	5	20	16	
Rivanna River Palmyra, Va.	4/17/60	76	7.0	15	24	12	

TABLE 2

Zinc Concentration and pH of River Waters in the Southeastern United States

Location of Sample Station	Date of Sampling	Zinc (Zn^{++}) Concn.—*ppb*	pH
Nassau River, at bridge on US Rte. 17 in Florida	4/7/61	64	7.4
St. Mary's River, on US Rte. 17 at Georgia-Florida border	4/7/61	66	6.9
Santee River at bridge on US Rte. 17 in South Carolina	4/8/61	36	7.3
Roanoke River near US Rte. 301 at Weldon Hatchery, Weldon, N.C.	4/9/61	37	7.7

bearing wastes near Danville, Pa., and the zinc content increases to 120–155 ppb. Just 2½ mi below this point, samples taken the same day show only 45 ppb zinc. Gunpowder Falls samples exhibit zinc levels ranging from 34 to 115 ppb. Abandoned mines and quarries may account for these values, as there are no industrial discharges upstream of the sampling point.

Maryland's Eastern Shore

The rivers of the eastern shore of Maryland, the Choptank, Nanticoke, Pocomoke, Tuckahoe, and Wicomico are all quite similar in character. They originate in low, marshy regions that are high in organic content, they flow in sandy channels, all exhibit low pH and low alkalinity, are very soft, and have comparable amounts of zinc in solution. The range of zinc concentrations at the time of sampling is a rather narrow 55–95 ppb.

Potomac River Basin

Emphasis in this study was placed on the Shenandoah and Potomac rivers. Substantial dolomite and limestone deposits in this region promote high alkalinity, pH, and hardness. In addition, the discharge of wastes from rayon tire cord manufacturing contributes zinc to the system in the area of Front Royal, Va. Despite the discharges of zinc-bearing wastes, the concentrations of zinc (ranging from 12 to 92 ppb and averaging 34 ppb) found in these waters were generally much lower than the average for the region as a whole. This would tend to indicate that, as zinc concentrations are far below saturation levels in all areas, the alkaline streams contain less zinc than neutral or acid streams, owing to mechanisms other than solubility alone.

Region South of Baltimore

The rivers south of Baltimore can be roughly classified as neutral in pH

TABLE 3

Zinc on Bottom Solids Collected From Streams of the Chesapeake Bay Region

Location of Sample Station	Date of Sampling	Zinc Content per Gram of Solids—*μg*
Big Gunpowder Falls Perry Hall, Md.	3/9/60	398
Potomac River Harper's Ferry, W. Va.	3/13/60	400
Point of Rocks, Md.	3/13/60	152
Shenandoah River Harper's Ferry, W. Va.	3/13/60	514
South Branch Front Royal, Va.	4/11/60	103
Potomac River Dalecarlia Treatment Plant Washington, D.C.	6/4/61	100

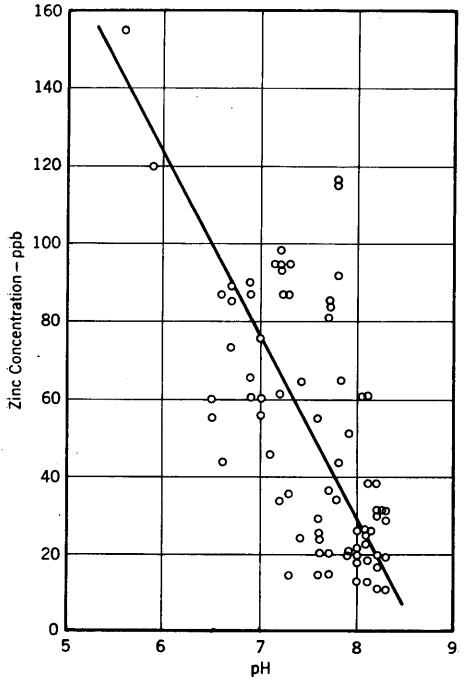

Fig. 2. Relation of Zinc Concentration in Natural Waters and pH

A general relationship is evident, as the zinc concentrations of the more alkaline waters are markedly lower than those of the neutral waters.

and low in alkalinity and hardness. Observed zinc levels fall in the range of 15–95 ppb.

The average zinc level of each subregion, computed as the mean of the samples taken, was 70 ppb north of Baltimore, 78 ppb for Maryland's eastern shore, 34 ppb in the Potomac River Basin, and 70 ppb south of Baltimore. The overall mean zinc content of the samples taken was 50 ppb. This average is biased towards the low side, as many more samples were taken in the region of lowest zinc content than in the other regions. The quantities of zinc found were always well below those given in the USPHS Drinking Water Standards,[7] which recommends an upper limit of 5 ppm.

All the rivers sampled terminate in the Chesapeake Bay. Zinc concentrations found in the alkaline, brackish Chesapeake Bay were less than those found in the streams. These concentrations are usually within the 5–15-ppb range.

Discussion

The solubility of zinc in distilled water is governed by the zinc hydroxide or zinc carbonate equilibriums. Zinc salts precipitated from supersaturated solution are reported to be mixtures of carbonate and hydroxide, described as the basic carbonate (Fig. 1).

TABLE 4

Measured Solubility of Zinc at Various pH Values in Shenandoah River Water at 20°C

pH	Zinc Concn.—*ppm*
7.5	25.0
8.0	3.5
8.5	0.8
9.0	0.4

Comparison of the zinc levels of natural waters with the solubility of zinc as the carbonate and as the hydroxide shows that the concentrations of zinc found in natural waters are well below these solubility limitations (Fig. 2). In addition, the solubility of zinc in Shenandoah River water was determined. The results are shown in Table 4.

These values compare reasonably well with those predicted from the solubility of zinc as the hydroxide in distilled water.

The zinc concentrations of the Chesapeake Bay tributaries are plotted against pH in Fig. 2. A general relationship is evident, as the zinc concentrations of the more alkaline streams

TABLE 5

Average Zinc Concentrations Found in Various pH Ranges

pH Range	Avg. Zinc Concn.—*ppb*
6.5–6.9	73
7.0–7.4	65
7.5–7.9	45
8.0–8.3	26

are markedly lower than those of the neutral streams.

The relationship between zinc content and pH is also evident from the data in Table 5, which gives average zinc concentrations found in various pH ranges.

The decrease in zinc concentration with increasing pH is attributed to increased absorption on river silts at higher pH. Such behavior was also observed with river silts in the laboratory, where the adsorbed zinc equilibriums were found to be easily and rapidly reversible with pH. This would also explain, at least in part, the observation that zinc concentrations found in the more alkaline Chesapeake Bay are lower than those found in the streams flowing into the bay.

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