Soluble–Adsorbed Zinc Equilibrium in Natural Waters

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TO evaluate the effect on a stream of both the discharge of zinc waste and the continuous addition of small quantities of radioactive zinc, the factors that influence the quantity of zinc in natural waters must be considered. The relative insolubility of the salts zinc carbonate and zinc hydroxide, place an upper limit on the quantities of zinc found in natural waters. It is possible, therefore, because the quantities of zinc found in natural waters are one or two orders of magnitude below the solubility limits, that most natural water systems are merely undersaturated with respect to zinc. There is evidence, however, that indicates that the quantities of zinc found in solution are related to other factors. This evidence shows that:

1. Zinc disappears rapidly from undersaturated solutions at points downstream from where it is discharged by industry. The river silts in such areas have high zinc contents.[1,2]

2. The zinc concentrations of natural waters are found to decrease with increasing pH.[3]

The study of zinc in natural waters was undertaken, therefore, to examine the effects of varying solids (silt) concentration and varying pH on the quantity of zinc in solution. Because the influence of these factors on the soluble–adsorbed zinc equilibrium was initially unknown, research was begun using controlled laboratory experiments.

Test of Freundlich Isotherm

Those factors that may have a distinct influence on the soluble–adsorbed zinc equilibrium are:

1. The total zinc content (or concentration of the zinc ion)

2. The concentration, particle size distribution, and physical properties of the suspended solids

3. The concentration of the hydrogen ion and the other ions that might compete for the adsorption sites on the solids.

One approach to the description of adsorption equilibria is the empirical Freundlich adsorption isotherm, $y = kc^{1/n}$ in which y is the quantity of material adsorbed per gram of adsorbent and c is the equilibrium concentration of the material being adsorbed, whereas k and n are empirically derived constants. The isotherm, although widely used, is not wholly adequate to describe the zinc equilibria in natural waters because it does not provide for the expression of any pH dependence.

Therefore, a means for describing the soluble–adsorbed zinc equilibria was sought that would relate the major variables to the concentration of zinc in solution. For limited ranges, this

objective could be realized using ordinary regression techniques and by formulating an equation relating the zinc in solution to pH, silt content, and total zinc content of the system. Although such an equation could provide a neat mathematical picture, it ignores the fact that a river system is exceptionally variable in other respects. The solids collected are only one small sample of the particles in an entire stream. Along a stream there will undoubtedly be solids with high- and low-adsorption or exchange capacities, high- and low-
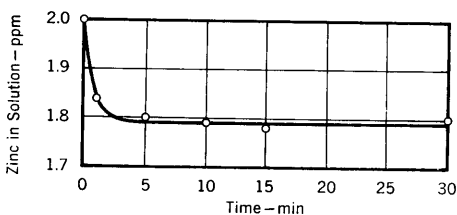

Fig. 1.　Rate of Attainment of Soluble–Adsorbed Zinc Equilibrium

The graph shows the results of an experiment in which 10-ml samples of water containing 100 ppm of suspended solids to which 2 ppm zinc had been added, were run through a membrane filter. With adequate stirring, equilibrium was rapidly attained.

organic contents, and high and low surface-to-volume ratios. In addition, the results for one watercourse may not be transferable to another watercourse or even to another reach of the same watercourse. In nature, the zinc content, as well as the pH, may vary from hour to hour and depth to depth. From these considerations it appeared best to examine the phenomena involved empirically and to test a wide variety of systems so as to determine what variation in effects might be anticipated.

Rate of Equilibrium Attainment

Initially, steps were taken to determine the rate at which soluble–adsorbed zinc equilibrium was established. The concentration of zinc in Shenandoah River water containing 100 ppm of suspended solids was increased to 2 ppm. Zinc-65 was added as a radioactive tracer. Prior to the addition of the zinc, the pH had been adjusted to 7.6, from 8.4, to prevent the metal's precipitation. After gentle swirling to provide contact, zinc samples of 10 ml each were filtered through 0.45-μ membrane filters at intervals of 1, 5, 10, 15, and 30 min. The results are shown in Fig. 1.

From these and many other observations, it appears that equilibrium is attained quickly when adequate stirring is provided. Furthermore, it was learned that if the pH is returned to the starting value, the amount of zinc adsorbed will also return to that point. In other words, the procedure is completely and rapidly reversible. When a zinc precipitate is formed, however, the solution tends to be buffered at pH 9.0. Reestablishment of equilibrium at another pH is difficult, therefore, and requires prolonged, vigorous stirring and successive additions of acid.

Zinc Concentration and Adsorption

In an effort to determine whether the soluble–adsorbed zinc equilibria followed a form of the Freundlich isotherm, various concentrations of tracer zinc were added to a sample of Shenandoah River water, taken at Harpers Ferry, W. Va., and containing 171 ppm suspended solids. The pH was adjusted to 7.3 to prevent precipitation and the samples were brought to equilibrium.

After filtering and analysis, the percentage and concentration of zinc remaining in solution, as well as the quantity adsorbed on the solids, were

computed. The results are shown in Table 1. A log-log plot of the milligrams of zinc adsorbed per gram of dry solids, against the equilibrium zinc concentration has the linear Freundlich form in the range of 1–10 ppm zinc. The plot and the straight-line approximation used to estimate the adsorption isotherm are shown in Fig. 2. Evaluation of the coefficient yields the isotherm $y = 1.59 \, c^{0.614}$ for pH 7.3. In this equation, y represents milligrams of zinc per gram of solids, and c is the parts per million of zinc in solution.

An indication that the adsorption phenomena were believed to exert a great influence on the amount of the substance found in solution in this region. To start with, then, water and silts were selected from the Shenandoah River at Harpers Ferry, W. Va. Here, the pH is about 8.2; the alkalinity approximately 110 ppm, and the total hardness about 140 ppm. The zinc content of the water was recorded as 12, 18, and 61 ppb for different samples. The zinc content of the silt at this site was recorded as 514 μg zinc per gram of solids, the highest value recorded in the Chesapeake Bay region.

TABLE 1

Results and Calculations for Estimating Adsorption Isotherm for Zinc Adsorption*

Test Number	Zinc—*ppb*						x/m† After Addition	Log x/m†	Log c‡ *ppm*
	In Water	On Solids	Added	Total	c Zinc in Solution, After Addition	Zinc on Solids, After Addition			
1	60	87	224	371	188	183	1.07	0.0294	−0.726
2	60	87	468	615	436	179	1.05	0.0212	−0.361
3	60	87	1,132	1,279	1,020	259	1.51	0.176	0.0086
4	60	87	2,263	2,410	2,020	390	2.28	0.358	0.305
5	60	87	5,670	5,817	5,060	757	4.44	0.647	0.704
6	60	87	11,320	11,467	10,370	1,097	6.43	0.808	1.016

* The sample was made on Mar. 13, 1960, from the Shenandoah River at Harpers Ferry, W. Va. The adjusted pH was 7.3. 171 ppm solids were added.
† Milligrams of zinc per gram of solids.
‡ The form of the Freundlich isotherm used is $x/m = kc^{1/n}$ or $\log x/m = (1/n) \log c + \log k$.

equilibria behave regularly is that an adsorption isotherm can be used to approximate the concentration dependency. It is clear that at total zinc concentrations below 1 ppm, the percentage of zinc adsorbed may be quite large. In natural water systems, therefore, when zinc concentrations are well below 1 ppm, the major portion of the zinc in the system may be adsorbed when equilibrium exists.

Solids and pH Concentration

Because the quantities of zinc found in the Potomac River Basin were low, To estimate the effect of pH and solids concentration on the fraction of zinc in solution, the total zinc content was held constant at 2 ppm. That is, the total amount of zinc in a water-solids system that included adsorbed zinc, zinc in the initial water sample, added stable zinc, and added tracer zinc, equalled 2 ppm.

Using Shenandoah water with 2 ppm total zinc, solutions containing 15, 35, 78, 170, 476, and 858 ppm solids, respectively, were placed in beakers and the pH adjusted successively from 6.5 to 8.0 in intervals of 0.5. Limitations

on the solubility of zinc prevented continuing beyond 8.0. After filtration, the fraction of the total zinc remaining in solution was determined by zinc-65 tracer counting.

The results, shown in Table 2, demonstrate that pH, as anticipated, has a very definite effect on zinc adsorption. This result indicates an exchange between zinc and the hydrogen ion. All the zinc can be removed from the solids
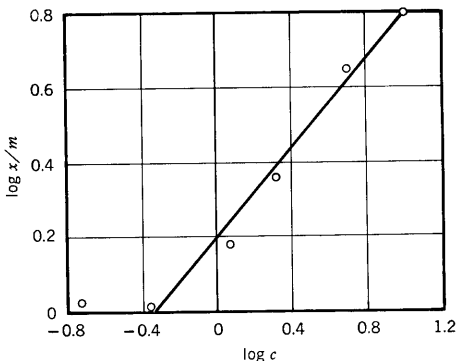

Fig. 2. Log-Log Plot and Straight-Line Approximation of Adsorption Isotherm

The graph shows that a plot of the milligrams of zinc adsorbed per gram of dry solids against the equilibrium zinc concentration, assumes the linear Freundlich form, in the range of 1–10 ppm zinc. The value of x/m in the diagram is 1.59 $c^{0.614}$. The pH is 7.3. The solids are from the Shenandoah River. See Table 1 for the complete results of the experiment.

by adjusting the pH to the pH 3–4 range. (This adjustment was commonly made after the tests were completed, as a check on the total zinc content.)

As the suspended-solids loads are usually less than 25 ppm in the Shenandoah River, little zinc would be adsorbed from the main body of the stream. Where the solids concentration is high, however, as in the stream bed, the removal of zinc from solution,

even at levels as high as 2 ppm, might be virtually complete.

A linear-regression analysis was run on the data appearing in Table 1 in order to construct an expression that would replace the adsorption isotherm and include the pH dependency. The result of this analysis appears as Eq 1.

Fraction of zinc in solution
= 2.48 − 0.125 (pH)
   − 0.445 log (ppm solids)
95 per cent confidence limits, ± 0.176   (1)

The entire experimental procedure was repeated with Shenandoah River

TABLE 2

Effect of pH and Solids Concentration on Zinc Adsorption—Shenandoah River, Harpers Ferry, W. Va.

pH	Solids Concentration—*ppm*					
	15	35	78	170	476	858
	Fraction of Zinc not Adsorbed*					
6.5	0.977	0.950	0.833	0.820	0.569	0.370
7.0	0.972	0.930	0.826	0.691	0.310	0.225
7.5	0.980	0.895	0.808	0.593	0.286	0.181
8.0	0.915	0.867	0.739	0.568	0.211	0.092

* Original zinc concentration was 2 ppm.

water and solids from the South Branch, Shenandoah River, above Front Royal, Va., to provide a comparison between different water-solids systems taken from the same watercourse. The pH range was increased and higher solids contents were chosen in order to simplify the analysis and increase the significance of the results shown in Table 3 and Eq 2.

Fraction of zinc in solution
= 2.17 − 0.165 (pH)
   − 0.315 log (ppm solids)
95 per cent confidence limits, ± 0.086   (2)

As can be seen, the resulting linear expression for the South Branch of

the Shenandoah River is similar to the expression computed previously.

Variations in Adsorptive Capacity

To determine further whether different water-solids systems varied in adsorptive capacities, five water-solids systems were compared. Equal quantities of water, plus solids from each region, were used in these tests. The suspended-solids concentration was 100 ppm. The zinc content of each system was augmented so that the total zinc content was 200 ppb. Holding these factors constant, the pH was varied and the resulting curves showing zinc in solution against pH (Fig. 3) provided a comparison between solids.

As Fig. 3 shows, similar curves were obtained with solids from the Shenandoah River at Harpers Ferry, the Potomac River at Harpers Ferry, the Big Gunpowder Falls at Perry Hall, Md., the Potomac River at Point of Rocks, Md., and the Shenandoah River at Front Royal, Va. In fact, it appeared that zinc adsorption is nearly independent of the source and nature of the solids used.

These tests were also used to determine the influence of other factors. Whereas the equilibria were generally reversible, it was learned that if pH 8.4 was exceeded, the equilibrium curve shifted to a lower, but parallel, position. Evidently, some colloidal zinc forms when the limit of zinc solubility is approached. This material is not easily redissolved unless the pH is returned to a level below 6.0. The formation of the colloidal zinc probably takes place because of the local excess in pH that occurs when sodium carbonate is added to the solution for pH adjustment.

The large error evident from the scatter of points used to estimate the curves in Fig. 3 should be expected on the basis of the confidence limits computed earlier. The error does not seem to be inherent in the system, however, but in the experimental procedures. This fact became clear when a very rigorous filtering procedure was adopted. As a result, the curves in Fig. 3 (e) show less scatter than the other curves.

For one series of tests, sodium hydroxide, rather than sodium carbonate, was used for pH adjustment. The resulting curve was the same, but it took longer and more vigorous stirring to reach equilibrium conditions.

TABLE 3

Effect of pH and Solids Concentration on Zinc Adsorption—South Branch, Shenandoah River, Front Royal, Va.

pH	Solids Concentration—*ppm*			
	85	208	458	1,025
	Fraction of Zinc not Adsorbed*			
5.5	0.904	0.820	0.697	0.549
6.0	0.854	0.762	0.603	0.436
6.5	0.758	0.645	0.454	0.353
7.0	0.678	0.483	0.441	0.291
7.5	0.525	0.498	0.356	0.277
8.0	0.402	0.404	0.327	0.196

* Original zinc concentration was 2 ppm.

Zinc adsorption, as indicated by the results of the regression analysis, appears to be a logarithmic function of solids concentration. This indication is supported by the two curves shown in Fig. 3 (d) for 100- and 200-ppm solids concentrations.

The calcium ion, which is the most abundant cation in many natural water systems, has only a limited effect on zinc adsorption. This finding is demonstrated in Fig. 3 (e). The South Branch of the Shenandoah River initially contained 27 ppm Ca^{++}. An additional 40 ppm Ca^{++} was added to
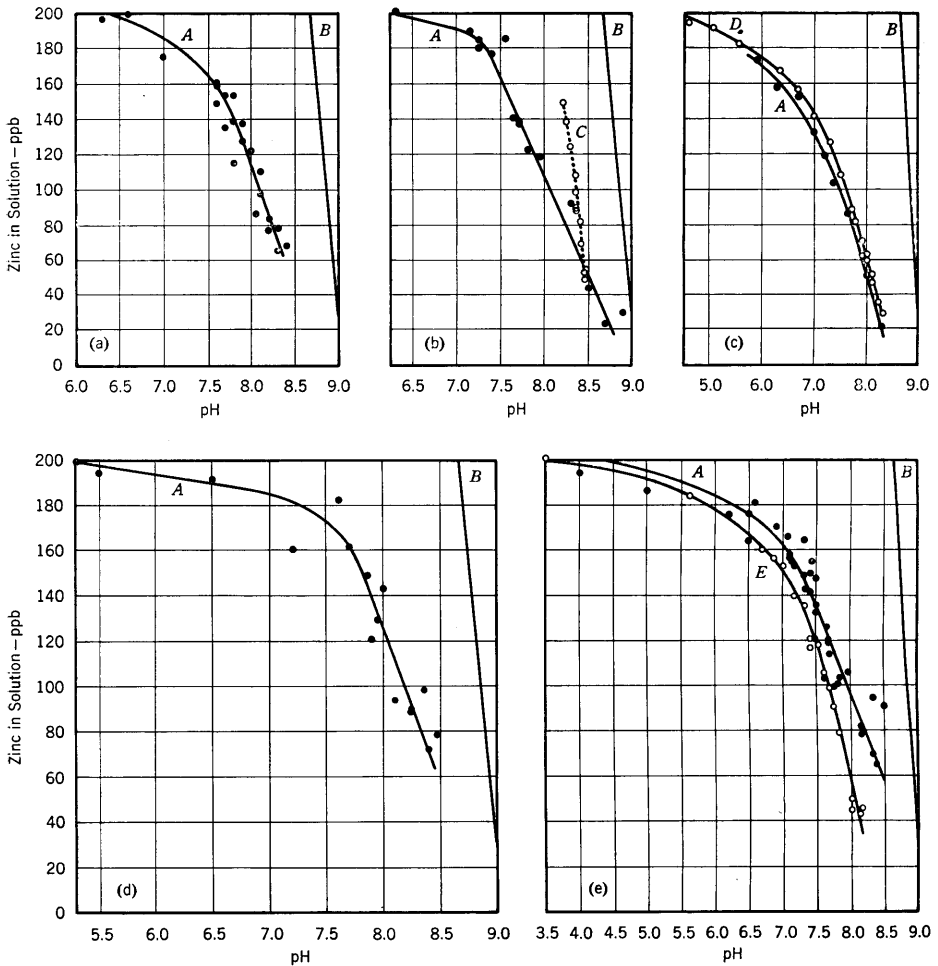
Fig. 3. Adsorptive Capacities of Five Different Water-Solids Systems

Each system tested contained a suspended-solids concentration of 100 ppm and a total zinc content of 200 ppb. These factors were held constant and the pH varied. The resulting curves, designated as A, showing behavior of the zinc in solution, are quite similar. The lines marked B represent the limit of zinc solubility as zinc hydroxide. The designation, C is for the curve representing the exchange of tracer zinc-65 with previously adsorbed zinc. The curve marked with a D shows the effect of adding 40 ppm calcium ion to the system. Finally, the line designated E represents the reaction of 200 ppm solids. The test areas represented by the graphs are: (a) Shenandoah River, at Harpers Ferry, West Va., (b) Potomac River, at Harpers Ferry, W. Va., (c) South Branch, Shenandoah River, above Front Royal, Va., (d) Big Gunpowder Falls, at Perry Hall, Md., and (e) Potomac River, at Point of Rocks, Md.

the water being tested after the curve for 100 ppm added solids had been determined. The resulting solution was studied more intensively than the first one, and a small difference may be observed between the two curves. As a result, it appears that the zinc adsorption is relatively insensitive to the calcium ion concentration in the range tested.

One further interesting result is illustrated by the dashed curve in Fig. 3 (b). Zinc-65 tracer was added following the addition of the stable zinc instead of along with the stable zinc. With stirring, the zinc-65 was seen to enter the zinc equilibrium after 2 hr. This observation would seem to confirm the earlier indication that the equilibrium is easily and rapidly reversible.

Acknowledgment

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