

Acid Rain, pH & Acidity: A Common Misinterpretation

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We cannot use pH as a measure of acidity. A number of introductory biology, ecology and environmental science texts would have us believe otherwise by suggesting there is a simple and straightforward relationship between pH and acid content. Many texts make a general statement that the lower the pH, the higher the acidity (Miller 1988, p. 192-193; Wallace, King & Sanders 1986, p. 45; ReVelle & ReVelle 1988, p. 494).

More specifically, we are told that a decrease in pH by one unit corresponds to a 10-fold increase in acidity (Wessels & Hopson 1988, p. 42; Andesirk & Andesirk, 1986, p. 51).

This common misinterpretation is often applied to the acid rain phenomenon, giving rise to misleading statements implying that acid rain can be as acid as lemon juice (Maxwell, Mansfield-Jones & Mansfield-Jones 1985, p. 185), or 1,000 times as acid as normal rain (Wessels & Hopson 1988, p. 1098; Barrett, Abramoff, Kumaran & Millington 1986, p. 1054). A current ecology text notes that rain at a record low pH of 1.4 is 15,800 times as acid as normal rain at pH 5.6 (Brewer 1988, p. 800). This latter example leads us to envision an explosive and unrealistic surge in acid production by industrial giants. The correct increase in acidity would probably be about 2,000 to 4,000 times—not 15,800—for a change in rain pH from 5.6 to 1.4. In this paper we illustrate the basis for such misleading statements and explain why pH cannot be used as a measure of acidity for rain or any other solution.

The tendency to link pH to acidity is understandable, but not justified since acidity and pH are defined very differently. The pH is equal to the negative logarithm of the molar hydrogen ion concentration: $\text{pH} = -\log[\text{H}^+]$. Acidity is properly defined as the concentration of acid determined by titration with a strong base to a specified end point (often the

phenolphthalein end point). Acidity refers to the concentration of titratable acid, but not to the H^+ concentration produced by the acid.

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To show that acidity is not determined by pH, compare 0.050 M hydrochloric acid (HCl) to 0.050 M acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$). One liter of each acid requires 0.050 mole of NaOH for titration to the phenolphthalein end point, thus the acids have the same acidity, which may be expressed as 0.050 M. But the acids do not have the same pH.

For the strong acid HCl, which is 100 percent dissociated, the pH is $-\log(0.050) = 1.3$. But for the weak acid $\text{HC}_2\text{H}_3\text{O}_2$, which is only about 1.9 percent dissociated, the pH is $-\log(0.019 \times 0.050) = -\log(0.00095) = 3.0$. The acids have different pHs but equal acidities, a fact which can be easily verified in simple lab titrations.

Why is the statement often made that a decrease of pH by one unit corresponds to a 10-fold increase in acidity (we will refer to this as the "one-for-ten" rule)? This is correct only for strong monoprotic acids such as HCl. As we increase the concentration of HCl from 0.050 M to 0.50 M by adding more HCl, the pH changes from 1.3 to 0.3, which gives us the expected one-unit decrease corresponding to the 10-fold increase in acidity.

But the "one-for-ten" relationship does not hold when we add HCl to acetic acid. Suppose we start with $\text{HC}_2\text{H}_3\text{O}_2$ at a concentration of 0.050 M and add enough HCl to increase the acidity 10 times. In the final solution the concentration of $\text{HC}_2\text{H}_3\text{O}_2$ would be 0.050 M and the concentration of HCl would be 0.45 M, giving a total concentration (i.e., acidity) of 0.50 M. By a LeChatelier effect the strong acid HCl sharply suppresses the dissociation of the weak acetic acid, and we may assume that essentially all the H^+ ions come from the HCl. The new pH would be $-\log(0.45) = 0.35$. So for this case, a 10-fold in-

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crease in acidity causes a pH decrease of about 2.7 units (3.0-0.35)—much greater than the erroneously expected one unit change.

If we add additional acetic acid to 0.050 M $\text{HC}_2\text{H}_3\text{O}_2$ to increase the acidity 10 times and result in a final concentration of 0.50 M, the percent dissociation of the acid will decrease to about 0.6 percent. The final pH will be $-\log(0.006 \times 0.50) = -\log(0.0030) = 2.5$. In this case the 10-fold increase in acidity corresponds to a pH decrease of only 0.5 unit (3.0-2.5)—much smaller than the erroneously expected one unit change.

Now let's look at the situation for rain water. Clean, or normal, rain is usually said to have an expected pH of 5.6 due to the presence of natural CO_2 , which dissolves from the air and hydrolyzes to form carbonic acid (H_2CO_3). The concentration of H_2CO_3 required to produce a pH of 5.6 is 1.8×10^{-5} M, which can be taken to be the total acidity of normal rain water. This acidity refers to titration by NaOH to the phenolphthalein end point, in which carbonic acid acts as a monoprotic acid. This is due to the fact that the bicarbonate ion (HCO_3^-) is too weak an acid to be neutralized by NaOH. We may thus neglect the very small amount of H^+ produced by the bicarbonate in normal rain water.

Let's suppose a sample of rain water has a pH of 4.6, one unit lower than the expected normal value of 5.6. Does this correspond to a 10-fold increase in acidity? The question is not easily answered. Noting that $[\text{H}^+] = 10^{-\text{pH}}$, we see that the hydrogen ion concentration has increased by a factor of 10 since $10^{-4.6}/10^{-5.6} = 10^{1.0} = 10$. We should not be surprised, since we know pH is in fact a measure of H^+ concentration.

But what has happened to the acidity of the rain water? If the culprit is HCl, then this strong acid would greatly suppress the dissociation of the original carbonic acid, and the pH of 4.6 would be due almost totally to the HCl. The concentration of HCl needed for this pH is $10^{-4.6} = 2.5 \times 10^{-5}$ M. Titration of the acid rain to the phenolphthalein end point would require 2.5×10^{-5} mole of NaOH per liter of rain to neutralize the HCl, plus 1.8×10^{-5} mole of NaOH for the carbonic acid initially present in the normal rain. Thus the total acidity would be the sum of the NaOH amounts, or 4.3×10^{-5} M. For this case of acid rain, the acidity has increased above normal by a factor of 2.4 times (since 4.3×10^{-5} M/ 1.8×10^{-5} M = 2.4), although the pH has decreased by one full unit. This again shows that pH change does not denote change in acidity.

Our last example is probably not very realistic, because it is generally accepted that it is sulfur oxides rather than HCl which represent the major cause of acid rain. Sulfur dioxide (SO_2) produced during fossil fuel combustion and ore roasting processes gets into

the air, where it dissolves in water droplets and hydrolyzes to form sulfurous acid (H_2SO_3), a weak acid. If the droplets contain oxidants such as oxygen, ozone or hydrogen peroxide and trace amounts of certain metals which act as catalysts, the SO_2 can rapidly oxidize to SO_3 . The sulfur trioxide hydrolyzes to form sulfuric acid (H_2SO_4), a strong acid. When dissolved in water, the sulfuric acid dissociates strongly to release H^+ and HSO_4^- ions. The bisulfate ion (HSO_4^-) is a much weaker acid than H_2SO_4 and does not contribute greatly to the hydrogen ion concentration. But it is strong enough that it is neutralized along with H_2SO_4 by titration with NaOH, so that sulfuric acid is definitely diprotic at the phenolphthalein end point. Thus, at least as a rough approximation, we can treat H_2SO_4 as a monoprotic strong acid when dissolved in water, but as a diprotic strong acid when titrated with NaOH. As in the case with HCl, the concentration of H_2SO_4 required for a pH of 4.6 is roughly 2.5×10^{-5} M. But upon titration with NaOH, the acidity becomes twice this (since the H_2SO_4 titrates as a diprotic acid), and the total rain water acidity becomes $2 \times 2.5 \times 10^{-5}$ M + 1.8×10^{-5} M = 6.8×10^{-5} M (approximately). For this case of sulfuric acid rain, the pH has decreased by one unit, but the acidity has increased by a factor of approximately $6.8 \times 10^{-5}/1.8 \times 10^{-5}$, or 3.8. Once again, the pH change cannot be used as a measure of the change in the rain water's acid content.

It is not unusual to observe rain at a pH of 2.6 or lower. What happens to the acidity for such a drastic drop in pH from 5.6 to 2.6? The $[\text{H}^+]$ increase is $10^{-2.6}/10^{-5.6} = 10^{3.0} = 1,000$ times, and some textbooks would have us believe the rain water has become 1,000 times as acidic as normal. But we can show by the previous methods of calculation that the increased acidity would be only 140 times if the offending acid is HCl, and roughly 280 times if sulfuric acid is the culprit. For an actual 1,000-fold increase in acidity due to HCl, the pH would decrease from 5.6 to $-\log(1,000 \times 1.8 \times 10^{-5}) = 1.7$, a much greater drop than from 5.6 to 2.6.

A major and very broad environmental implication of the correct interpretation of acidity and pH is that an industry does not have to increase its acid-gas production in rain water by 1,000 times, but only by 140 to 280 times, to bring about a drastic drop in rain pH by three units. Thus it appears that rain pH is generally more sensitive to increased acidification than is implied by the erroneous "one-for-ten" rule expressed in a number of texts. As stated in our opening paragraph, a record low rain pH of 1.4 can be obtained by increasing rain acidity by about 2,000 to 4,000 times, not by the mistakenly expected factor of 15,800.

A specific biological implication is shown when we attempt to consider the effect of pH and acidity on

aquatic organisms. For example, the hatching success of wood frog embryos in "Reconstituted Soft Water" acidified with sulfuric acid drops off sharply as the pH decreases below 4 (Pierce 1987). But does this clearly indicate a relationship between acidity and hatching success? The question goes to the heart of our point that pH cannot be used to denote acidity. Let's examine this point more closely.

If we use the incorrect "one-for-ten" rule, a pH drop from 5.6 to 4.0 would seem to imply that the acidity has increased by a factor of $10^{-4.0}/10^{-5.6} = 10^{1.6} = 40$ times. This, in turn, appears at first glance to imply that the frog embryos have a 40-to-1 "safety factor"; i.e., they do not encounter severe difficulties until the amount of acid dumped into their environment reaches 40 times the amount required for a relatively healthful pH of 5.6.

But as we have shown, this reasoning is flawed. To obtain a pH of 4.0 in normal rain water by adding HCl requires a concentration of HCl of $10^{-4.0} = 1.0 \times 10^{-4}$ M. Given an initial carbonic acid concentration (as stated before) of 1.8×10^{-5} M for a normal rain pH of 5.6, the total acidity at pH 4.0 would be 1.0×10^{-4} M + 1.8×10^{-5} M = 1.2×10^{-4} M. This is an increase in acidity by a factor of $(1.2 \times 10^{-4}/1.8 \times 10^{-5}) = 6.7$ times. Thus the "safety factor" in this case is only 6.7, not 40. This illustrates that perhaps the frog embryos are considerably more sensitive to the amount of acid in their environment than is implied by the "one-for-ten" rule. We may need to add only 6.7 times as much acid—rather than 40 times as much—to produce a sharp drop in hatching success.

There is, of course, a significant problem in this last illustration in terms of its applicability to a natural pond environment. The example assumes the addition of HCl to normal rain water. But a pond is unlikely to be only a 1.8×10^{-5} M solution of carbonic acid. And it is likely to contain many other substances, including some weak organic acids, perhaps some sulfuric acid from mine drainage, and metal ions such as aluminum, all of which will act in complex ways to modify the pH change imposed by the addition of HCl or any other acid to the pond. In fact, as pointed out by Pierce, it is not a simple matter to predict how pond water pH will be affected by acid rain.

We hope our examples have shed some light on a common misinterpretation of the relationship between pH and acidity. We must point out that the acid rain phenomenon is more complicated than our simplistic approach would imply. For example, we (and most texts) have assumed that the pH of normal rain is 5.6. But even trace amounts of natural gases

such as ammonia (NH_3) can sharply alter rain pH. It takes an air concentration of only 0.0039 parts per million of NH_3 to raise the pH of pure water by 1.4 units, whereas the same size decrease in pH requires an air- CO_2 level of 320 ppm. Thus NH_3 is roughly 80,000 times as effective as CO_2 in altering the pH, and an extremely small amount of ammonia in normal rain will produce a pH significantly higher than 5.6.

It should also be noted that almost all pH calculations are based on the standard reference temperature of 25 degrees Celsius (298 Kelvin), but rain is likely to be at lower temperatures, perhaps 15 degrees Celsius on average. At 15 degrees Celsius, pure water dissociates slightly less than at 25 degrees Celsius, and the pH of neutrality is 7.2 rather than 7.0. Use of pH values referenced to 25 degrees Celsius precludes exact calculations when applied to rain at lower temperatures (although exact calculations are seldom warranted due to the complexities of acid rain chemistry and the limited reliability of pH readings taken in the field).

We think it would be desirable to avoid teaching that pH is a measure of acidity, and we believe teachers should abandon the idea that pH change corresponds in a straightforward way to change in acidity. Acidity and pH should be presented as two separate and distinct concepts. If we get the terminology correct, then we will be in a better position to understand and evaluate acid rain's impact on the environment.

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