The pH 5.6 Line of Acid Rain Belongs to the Rain, and the Damage to What Receives It

— Clean rain in equilibrium with **420** ppm of CO_2 has pH **5.598026**, and the line itself moves with CO_2, having fallen by **0.087873** since 280 ppm — the damage is set not by the pH of the rain but by the neutralizing capacity left in what receives it — [Paper 573]

Yuuki YAMAGISHI (山岸 勇輝)
Yamagishi Complexity Torus Lab, Japan
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— From thinking to syncing. —

Abstract

Acid rain is defined as rain below pH 5.6, and its damage is usually spoken of in terms of how acid the rain is.What this paper shows is that the line at 5.6 is a property of the rain set by atmospheric CO_2 and itself moves, while the damage is set not by the rain but by the neutralizing capacity left in the lake that receives it.No new theorem or law is claimed. First, the pH of clean rain is set by equilibrium with CO_2——at 420 ppm it is 5.598026; the "5.6" comes from here (Section 2). **Second, the line moves with CO_2——5.685899 at 280 ppm and 5.535643 at 560; from 280 to 420 ppm it fell by 0.087873** (Section 2). **Third, the gap to the closed form comes from the dissociation of water——the closed form gives 0.088046, off by 1.7×10^{-4}; removing the dissociation of water and CO_3^{2-} returns the closed form to 10^{-9}, which settles where the gap comes from** (Section 2). **Fourth, and this is the core.The pH of a lake barely moves until its neutralizing capacity nears zero, and there it falls off a cliff——pH 8.1898 at a capacity of 1000 μeq/L, 6.2213 at 10, 5.5980 at 0 and 4.5198 at -30** (Section 4). **Fifth, under the same rain, the acid a lake can take differs 214.7099 times——the acid needed to push below pH 6 is 994.6324 μeq/L for a capacity of 1000 and 4.6324 for 10, wider apart than the hundredfold ratio of capacities** (Section 4). **Sixth, the separator is whether a quantity belongs to the rain or to the receiver——the line is set by CO_2 and the damage by neutralizing capacity, two distinct roots** (Section 5). **Keywords**: acid rain, pH 5.6, carbonate equilibrium, acid neutralising capacity, lakes.

Scope of this paper (scope note): No new theorem or law is claimed——carbonate equilibrium and acid-neutralizing capacity are standard.Constants are representative values at 25 degrees——a Henry constant for CO_2 of $\log K_H = -1.47$, $\mathrm{p}K_1 = 6.35$ and $\mathrm{p}K_2 = 10.33$.A lake is treated as one box——exchange of water, adsorption of sulphate on soils and the rate at which weathering restores capacity are not included. “Acid added to the lake” is a thought experiment: the total strong acid added per litre of lake water.The sensitivity of living things is not treated ——pH 6 is a mark for comparison; where fish or algae are harmed is not stated, and dissolved aluminium is not included.The chemistry of rain is not exhausted——the raising of rain pH by ammonia or by calcium in dust is not included.Relation to earlier papers: Paper 569 showed that the higher the station, the more its sea-level pressure is an assumption——the line at 5.6 is of the same kind, a function of the assumed concentration of CO_2.Paper 408 showed that water evaporates and salt does not, so even drinkable water kills the land——the shared shape is that what is left in the receiver matters more than the nature of what goes in; there accumulating salt, here dwindling capacity.Paper 300 showed that sharing a root is decidable——“the line moves with CO_2” and “the damage is set by capacity” have distinct roots.What is added is solving the pH of clean rain exactly from the charge balance and comparing it with the approximate formula, settling the source of the gap between the shift **0.087873** and the closed form by solving again with terms removed, setting out the cliff in lake pH near zero capacity, finding the ratio **214.7099** of acid tolerated before pH 6 and showing why it opens wider than the ratio of 100 that was put in, and placing the separator on the distinction between the rain’s side and the receiver’s.

1. Notation and the Question

Setting: in water in equilibrium with atmospheric CO_2 at partial pressure p,

$$[\mathrm{H_2CO_3^*}] = K_H\,p, \quad [\mathrm{HCO_3^-}] = \frac{K_1[\mathrm{H_2CO_3^*}]}{[\mathrm{H^+}]}, \quad [\mathrm{CO_3^{2-}}] = \frac{K_2[\mathrm{HCO_3^-}]}{[\mathrm{H^+}]},$$

and solving the charge balance including the acid-neutralizing capacity ANC,

$$\mathrm{ANC} + [\mathrm{H^+}] = [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{OH^-}],$$

gives the pH.With ANC zero and only $[\mathrm{H^+}] = [\mathrm{HCO_3^-}]$ kept, it reduces to $\mathrm{pH} \approx -\tfrac{1}{2}\log_{10}(K_H K_1 p)$.

Observation 1.1

acid rain is defined as rain below pH 5.6.And its damage is usually spoken of in terms of how acid the rain is ——where the line comes from and what sets the damage are separate questions.

Question: what sets the line at 5.6?Why does the same rain do different damage to different lakes?

2. Clean Rain

Computation 2.1: the charge balance solved by bisection.

atmospheric CO_2	pH of clean rain
280 ppm	**5.685899**
420 ppm	**5.598026**
560 ppm	**5.535643**

> **Observation 2.2**
>
> checked against the approximation.At 420 ppm the approximate formula gives **5.598375**, within 0.001 of the exact solution——"5.6" is the pH of rain with nothing but CO_2 dissolved in it.

> **Observation 2.3**
>
> the line itself moves.From 280 to 420 ppm the pH of clean rain fell by **0.087873**——the same number "5.6" draws a line whose meaning moves with the atmosphere.

> **Observation 2.4**
>
> the gap to the closed form was settled by removing terms.The approximation gives the shift in closed form as $\frac{1}{2}\log_{10} 1.5 = \mathbf{0.088046}$. The first version of the check required this to match the exact shift to 10^{-4}, and it failed: the gap is 1.7×10^{-4}, and the fault was mine in fixing the threshold before measuring——rather than guess where the gap comes from, the system was solved again. Removing only the dissociation of water gives **0.088043819**, a gap of 1.8×10^{-6}; removing CO_3^{2-} as well returns the closed form to 10^{-9}. The gap comes almost entirely from the dissociation of water.

3. Rain with Strong Acid

Computation 3.1: strong acid (sulphuric or nitric) added to rain in equilibrium with 420 ppm.

strong acid added	pH
5 μeq/L	**5.2181**
10 μeq/L	**4.9747**
20 μeq/L	**4.6922**
50 μeq/L	**4.2999**

> **Observation 3.2**
>
> **on the rain's side a little acid moves a lot.10 μeq/L, about a hundred-thousandth of a mole of strong acid per litre, lowers the pH from 5.598026 to 4.9747——clean rain has almost nothing to take up acid.**

4. The Receiver's Cliff

Computation 4.1: **a lake in equilibrium with the same 420 ppm, with its acid-neutralizing capacity varied.**

ANC (μeq/L)	pH
1000	**8.1898**
300	**7.6713**
100	**7.1957**
30	**6.6760**
10	**6.2213**
3	**5.8430**
0	**5.5980**
−10	**4.9747**
−30	**4.5198**

> **Observation 4.2**
>
> **this is the core.Cutting the capacity a hundredfold, from 1000 to 10, lowers the pH by about 2, while moving it by only 40, from 10 to −30, lowers it about as much——the pH of a lake holds on until its capacity nears zero and then falls off a cliff. What sets the damage is not the pH of the rain but how much capacity the receiver has left.**

Computation 4.3: **the ANC at which the pH is exactly 6.0 is 5.367552 μeq/L (solving again with it returns pH 6.0 to 10^{-6}).**

Computation 4.4: **the acid that can be added before the pH falls below 6.**

lake	acid before pH 6 (μeq/L)
ANC 1000	**994.6324**
ANC 10	**4.6324**
ratio	**214.7099**

> **Observation 4.5**
>
> **the ratio opens wider than the capacities that were put in.The capacities differ a hundredfold, the acid tolerated 214.7099 times——the 5.367552 μeq/L needed to hold pH 6 eats half the margin of the small lake first. A poor lake is poorer than it looks.**

5. The Separator

> **Observation 5.1**
>
> **the separator is whether a quantity belongs to the rain or to the receiver.The line at 5.6 is set by atmospheric CO_2, on the rain's side; the damage by the lake's neutralizing capacity, on the receiver's——measuring only the rain cannot predict the damage.**

Observation 5.2

distinct roots, under Paper 300.“The line moves with CO_2” comes from the equilibrium of a dissolving gas; “the damage is set by capacity” from the shape of the receiver’s titration——changing one does not move the other.

Observation 5.3

the shape of Paper 569.There, the higher the station, the more its sea-level pressure became a function of the assumed temperature——here the line of acid rain is a function of the assumed CO_2. The reference value itself stands on an assumption.

Observation 5.4

the shape of Paper 408, in the same direction.There, even drinkable water killed the land as salt accumulated——what is left in the receiver matters more than the nature of what goes in: there accumulating salt, here dwindling capacity.

Observation 5.5

what is not said.It is not said that the pH of rain does not matter——it is the acid of that rain that wears the capacity down. What is shown is how differently the same rain harms different receivers, and where the number on the line comes from.

6. Roll Call and Closing

1. **clean rain at 420 ppm has pH 5.598026** (Computation 2.1): **where “5.6” comes from.**
2. **within 0.001 of the approximation 5.598375** (Observation 2.2): **two solutions compared.**
3. **the line moved by 0.087873** (Observation 2.3): **a function of CO_2.**
4. **the gap to the closed form 0.088046 is the dissociation of water** (Observation 2.4): **settled by removing terms.**
5. **pH 4.9747 with 10 μeq/L of strong acid** (Computation 3.1): **rain has nothing to take it up.**
6. **lake pH falls off a cliff near zero capacity** (Observation 4.2): **the core.**

7. **ANC at pH 6 is 5.367552** (Computation 4.3): **checked by solving again.**
8. **ratio of acid tolerated 214.7099** (Computation 4.4): **wider than the 100 put in.**
9. **the separator is rain or receiver** (Observation 5.1): **distinct roots.**
10. **the shape of Paper 569** (Observation 5.3): **a reference that stands on an assumption.**

Closing: **Acid rain is defined as rain below pH 5.6, and its damage is usually spoken of in terms of how acid the rain is.Yet the line at 5.6 is the pH of rain with nothing but CO_2 dissolved in it——rain in equilibrium with 420 ppm has pH 5.598026, within 0.001 of the approximate 5.598375; at 280 ppm it was 5.685899 and at 560 it would be 5.535643, so the line fell by 0.087873 from 280 to 420 ppm. The gap to the closed form 0.088046 is where the first check failed, its threshold fixed before measuring; solving again without the dissociation of water and CO_3^{2-} returns the closed form, which shows the gap comes almost entirely from the dissociation of water.The damage is set not by the rain but by what receives it——clean rain has so little to take up acid that 10 μeq/L of strong acid brings it to pH 4.9747, but a lake's pH holds on until its capacity nears zero and then falls off a cliff: pH 8.1898 at a capacity of 1000, 6.2213 at 10, 5.5980 at 0 and 4.5198 at -30. The acid tolerated before pH 6 is 994.6324 μeq/L for a capacity of 1000 and 4.6324 for 10, a ratio of 214.7099, wider than the hundred put in, because the 5.367552 needed to hold pH 6 eats the small lake's margin first.The separator is whether a quantity belongs to the rain or to the receiver——the line is set by CO_2 and the damage by capacity, and under Paper 300 the two have distinct roots.Placed among the earlier papers——as in Paper 569, a reference value stands on an assumed quantity. As in Paper 408, what is left in the receiver matters more than the nature of what goes in: there accumulating salt, here dwindling capacity.To be honest——the lake was a single box, with no exchange of water, no adsorption on soils and no restoring of capacity by weathering; the constants are representative values at 25 degrees; pH 6 is a mark for comparison, and where living things are harmed is not stated. Nor is it said that the pH of rain does not matter: it is the acid of that rain that wears the capacity down.**

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Yuuki YAMAGISHI (山岸 勇輝)

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