

## A double paradox in catchment hydrology and geochemistry

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The questions that we ask as scientists shape everything that follows. They can lead us to see the world in new ways, or mundane ones. They can spur the development of new approaches, or the recycling of established ones. They can focus our attention in useful directions, or leave us wandering aimlessly. In science, as in everything else, what you find will largely depend on what you were looking for.

Thus, sometimes one can be helpful simply by framing questions, even if—or *especially* if—the answers are not yet clear. My purpose here is to identify questions that I hope will be productive ones. I make no pretence of presenting answers. These questions have emerged from long hours pondering hydrochemical data like those shown in Figures 1 and 2. The same kinds of data have also been pondered by many others in our community, so I make no particular claim of originality for the observations that follow. I simply hope that presenting these observations in the following way may prove useful.

### Paradox 1: Rapid Mobilization of Old Water

The hydrology and biogeochemistry of small catchments present two linked paradoxes. The first is what I call the ‘rapid mobilization of old water’ paradox, exemplified by Figure 1. In many small catchments, streamflow responds promptly to rainfall inputs, but fluctuations in passive tracers (such as water isotopes and, in seasalt-dominated catchments, chloride) are often strongly damped. This indicates that storm flow in these catchments is mostly ‘old’ water (Neal and Rosier, 1990; Sklash, 1990; Buttle, 1994). The question that naturally emerges from time series like Figure 1 is this: *how do these catchments store water for weeks or months, but then release it in minutes or hours in response to rainfall inputs?*

Over the years, a variety of conceptual models have been invoked, with limited success, in attempts to resolve this paradox—piston flow, kinematic waves, transmissivity feedback, exchange between matrix and macropores, and so forth (Beven, 1989; McDonnell, 1990; Bishop, 1991; Kendall *et al.*, 1999). Proposing a conceptual model for prompt discharge of ‘old’ water is the easy part; the hard work lies in making such a model mechanistically plausible and quantitatively realistic. Many computer models successfully reproduce the flashy hydrographs observed in small catchments, but they usually do so by invoking flow mechanisms (such as Horton overland flow,

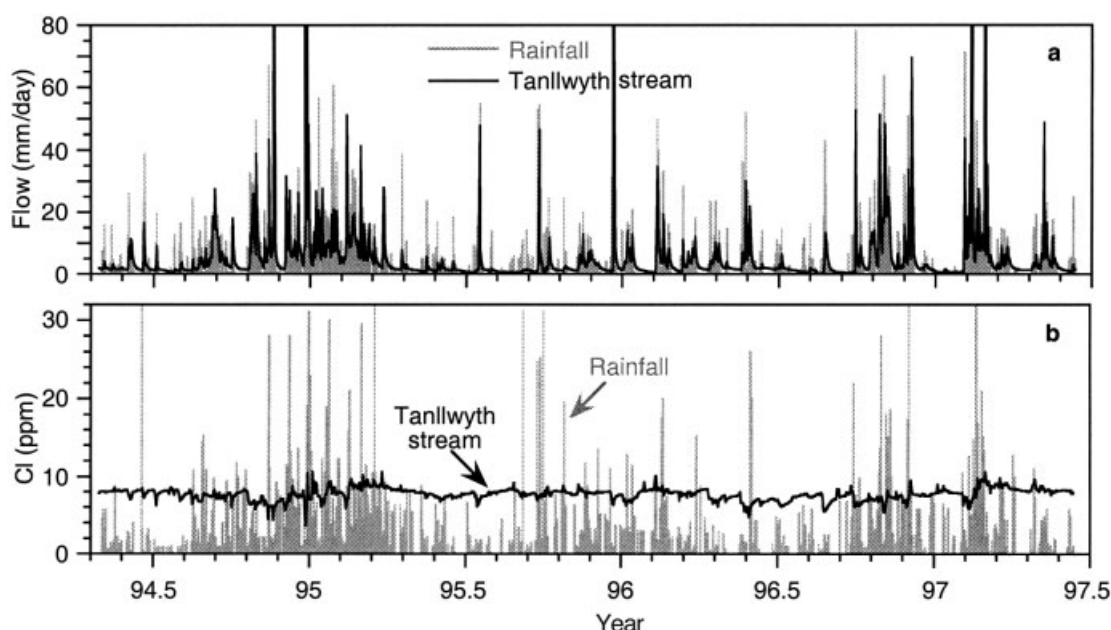


Figure 1. A 3 year record of daily water fluxes (a) and chloride concentrations (b) for Tanllwyth stream at Plynlimon, Wales; some high flows and concentrations exceed the range of the plots. Stream water fluxes respond promptly to rainfall inputs, but passive tracers in streamflow are strongly damped

saturation overland flow, or pipe flow) that imply that water fluxes and tracer concentrations in streamflow should *both* respond promptly to rainfall inputs (e.g. Neal *et al.*, 1988). That is indeed what happens in some catchments (Buttle *et al.*, 1995; Burns *et al.*, 2001). But what are we to make of the many cases like Figure 1, in which streamflow is highly responsive to recent rainfall, but passive tracers that move with the water are largely indifferent to recent rainfall? Perhaps the kindest thing one can say about the current state of knowledge is that the mechanisms by which catchments store water for extended periods, but then release it promptly during storm events, are not well understood.

## Paradox 2: Variable Chemistry of Old Water

Even in the absence of a solid mechanistic explanation, one could simply accept as an empirical fact that many catchments (somehow) store large volumes of 'old' water and release it promptly to the stream during storm events. But what makes this behaviour even more paradoxical is

that, as Figure 2 shows, concentrations of reactive chemical species (such as calcium, silicon, aluminium, or  $H^+$ ) are often highly sensitive to discharge. I term this the 'variable chemistry of old water' paradox: although baseflow and stormflow are both composed mostly of 'old' water, they often have very different chemical signatures. *How do catchments store 'old' water for long periods, but then release it rapidly during storm events, and vary its chemistry according to the flow regime?*

In other words, not all 'old' water is the same. One possible explanation is that chemical reactions rapidly reconfigure the chemistry of 'old' water as it is discharged to the stream, and they do so in different ways during baseflow and stormflow conditions. Another possibility is that catchments have several different stores (or a continuum of stores) of 'old' water, each with a different chemical signature, and these are mobilized in different proportions at high and low flows. The second explanation seems more plausible than the first, but in any case the physical and chemical mechanisms underlying both of these possibilities are poorly understood.

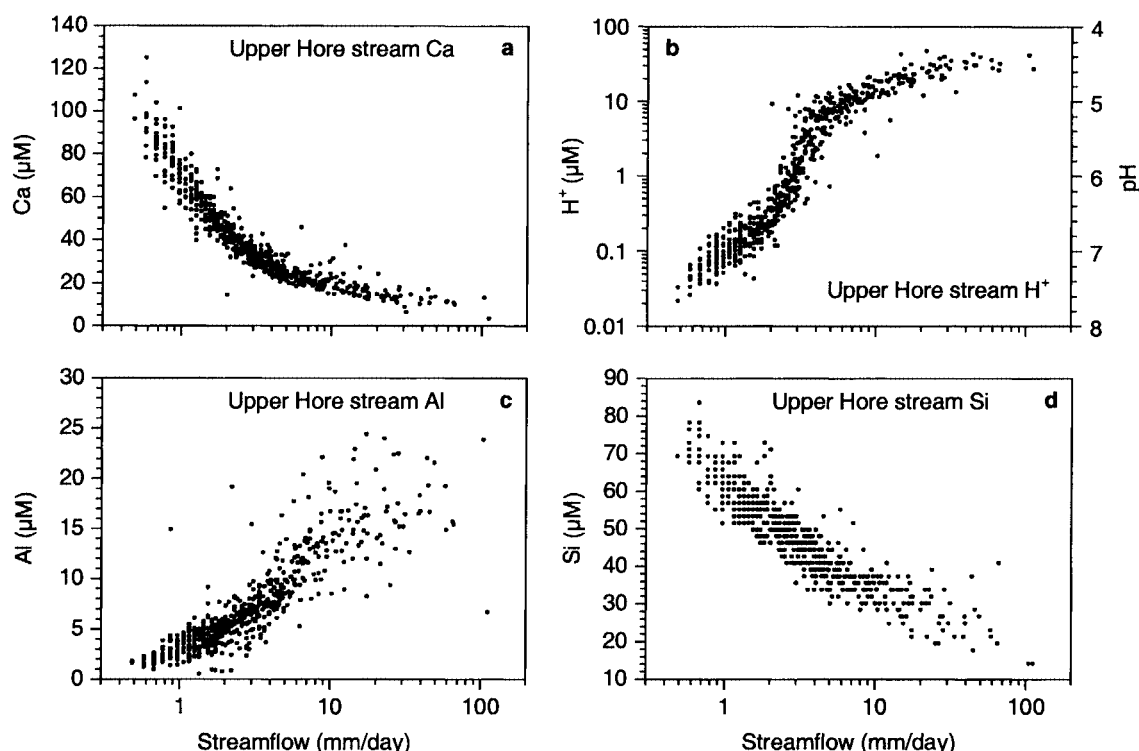


Figure 2. Concentrations of reactive chemical tracers as a function of streamflow for Upper Hore stream at Plynlimon, Wales. Reactive tracer chemistry depends strongly on flow regime, but the concentration–discharge relationship varies among different tracers

End-member mixing models have been invoked, with some success, to explain the variable chemistry of streamflow as a mixture of soil-water and groundwater pools (e.g. Hooper *et al.*, 1990; Genereux *et al.*, 1993). For example, one can envision the concentration–discharge relationships shown in Figure 2 as resulting from mixing between an idealized groundwater store (high calcium, high silica, low aluminium, low  $H^+$ ), which dominates at baseflow, and a soil-water store (low calcium, low silica, high aluminium, high  $H^+$ ), which dominates at high flows. Such a mixing model sharpens the puzzle but does not resolve it. How does the catchment store enough soil water to account for the large fluxes during high flow, if this soil water must also be ‘old’ from the standpoint of its passive tracer composition?

### The Search for a Unified Theory

As I said at the outset of this commentary, my objective has been to raise questions rather than

provide answers. Nonetheless, it is useful to consider what a satisfactory resolution of these paradoxes might look like. Because the phenomena outlined above characterize a wide variety of catchments, they demand a general explanation—an elegant theory rather than a highly parameterized megamodel. Obviously, separate explanations for each of these phenomena will not suffice. It is easy to envision models that can explain the prompt hydrologic response shown in Figure 1a, or the highly damped tracer response shown in Figure 1b, or the concentration–discharge relationships shown in Figure 2. What is much more difficult is to envision a single mechanistically plausible theory that can explain all three phenomena simultaneously!

We find ourselves in a situation similar to that of the 19th century physicists, who viewed mechanics, electricity, magnetism, heat, and light as separate phenomena obeying separate laws. The unification of physics is still a work in progress, but it has provided a remarkably powerful view of

the world. Without meaning to sound grandiose, I suggest that we need to take up the search for a unified theory, one in which we would no longer need to appeal to different—and often contradictory—conceptual models to explain physical and chemical phenomena that coexist in the same catchment. In a properly unified theory of catchment hydrology, the paradoxes outlined above would no longer seem paradoxical. The search for such a unified theory is likely to be difficult, but also instructive. It is a worthy challenge.

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