

## Resolving the Double Paradox of rapidly mobilized old water with highly variable responses in runoff chemistry

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### Introduction

The Double Paradox, presented by Jim Kirchner in *HP Today*, describes a set of issues that hydrologists have grappled with for decades. Despite all these efforts, Kirchner can provocatively claim that no satisfactory resolution has ever been provided that explains the rapid mobilization of old water with a variable runoff chemistry. We believe, however, that a resolution is possible for at least one case based on research at the Nyänget catchment in northern Sweden, where we have been working with precisely the issues that define the Double Paradox. While a full presentation of that work is being prepared, we think that a brief outline of our proposed resolution is an appropriate response to Kirchner's challenge that could help others to appreciate better the significance of the Double Paradox, and its resolution.

The chemistry of spring flood runoff from the 12 ha Västrabäcken on the Nyänget catchment is a textbook example of the double paradox (Figure 1). Isotope hydrograph separation indicates that spring runoff is over 60% 'old water', as flow rates increase by two orders of magnitude (Laudon *et al.*, 2002). The response of different chemical constituents is highly variable, from more than a halving of some constituents (such as Ca), to more than a tripling of others (e.g. dissolved organic carbon, DOC), while certain concentrations, such as that of Cl, remain quite stable (Hruška *et al.*, 2001).

How is the chemistry of water transformed along flowpaths through the catchment? And what do those flowpaths have to do with the variable chemistry of the 'old water' in stream runoff? To address these questions we have reduced the spatial dimensions of catchment hydrology and the origin of runoff chemistry to a representative two-dimensional hillslope scale. Several such transects have been studied at Nyänget. For the last several years, the one on the forested Västrabäcken subcatchment has been studied in detail, and this provides the basis for what we believe is a resolution of the Double Paradox.

### The proposed resolution

The resolution of the first paradox about how to mobilize so much old water so rapidly, is based on the transmissivity feedback mechanism. Although that term was coined to describe what was

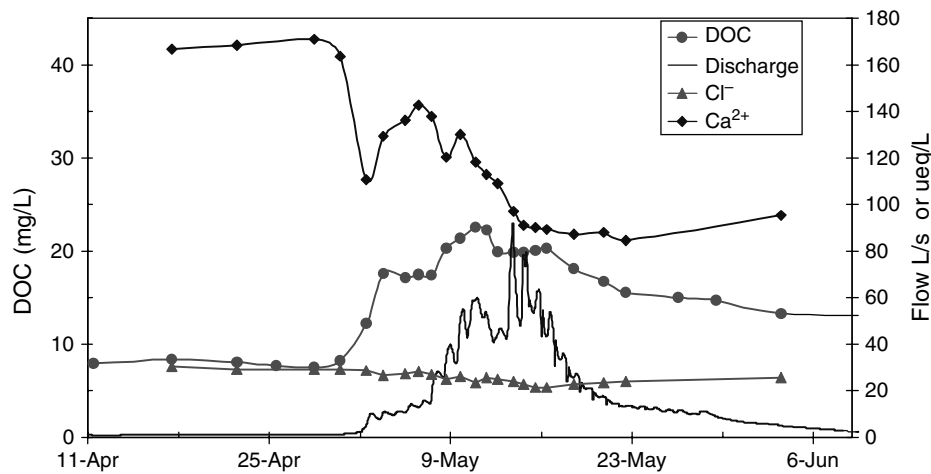


Figure 1. Spring flood from the Västrabäcken subcatchment of the Nyänget catchment in northern Sweden. The 12 ha subcatchment is comprised entirely of till soils, with podzols covering most of the subcatchment except for a band of organic-rich, riparian soils

seen in the Nyänget catchment (Bishop *et al.*, 1990), the term grows out of a long tradition of work on till soils that have a progressive increase in the lateral saturated hydraulic conductivity towards the soil surface (e.g. Tamm, 1931; Lundin, 1982; Rodhe, 1989). The addition of relatively little water causes the groundwater level to rise and, thus, to mobilize 'old' water held in the unsaturated zone. As the groundwater rises into highly conductive layers, large volumes of water can contribute to runoff events. The Nyänget transects exhibit a consistent groundwater-runoff relationship within some 30 m of the stream that can be explained in almost all situations with Darcy's law and without invoking bypass flow mechanisms. Interpretation of this relationship as the transmissivity feedback mechanism allows one to calculate the lateral flow contributions from each soil layer at a given runoff rate.

The resolution of the second paradox, the variable chemistry of old water, is explained by a juxtaposition of the lateral flow rates on the vertical profile of riparian soil solution chemistry (Figure 2). In the several thousand years since the glaciers retreated from the region, a distinct soil catena has developed, with podzols in the upslope areas covering most of the catchment and a localized zone of organic soils in the riparian zone at the base of the slopes. Both the upslope podzols and the riparian organic soils have distinct and persistent vertical patterns in soil solution chemistry

(Figure 3). Water moving downslope at the time scale of hours to days acquires the chemistry of the soil in the profile (at longer time scales the soils are, of course, themselves influenced by the amount and quality of water from upslope). With water's chemical evolution along flowpaths determined by the soil chemistry at any given point on its pathways, water entering the stream takes its chemistry from the riparian soils, which are the last soils in contact with the water before it becomes runoff. Lateral flow traversing the riparian zone gets the solution chemistry corresponding to the depth of its flowpath across the riparian zone. In this way, the riparian zone functions as a template that gives runoff a chemical signature that changes in a predictable way with flow, since different flow rates 'sample' the levels in the riparian soil profile in different proportions. (Bishop *et al.*, 1995).

We illustrate this with three types of chemical variability in episode runoff: Ca, DOC and Cl. Different riparian zone soil-solution concentration versus depth profiles for these chemical constituents give characteristic flow-concentration relationships that produce highly variable runoff chemistry in the old water mobilized during an event. The decrease in Ca concentration towards the soil surface (Figure 2) gives lower concentrations of Ca as flow increases when precipitation/snowmelt inputs of water to the soil progressively saturate (i.e. activate) more superficial flow paths.

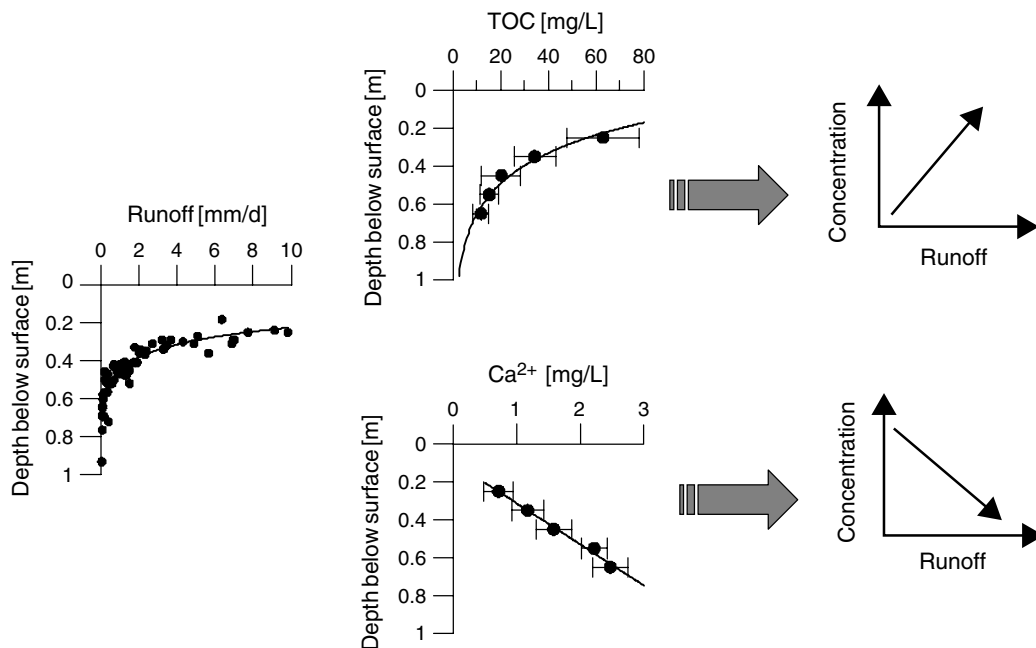


Figure 2. The conceptual framework for defining runoff chemistry as the integrated mixture of soil solutions ‘sampled’ by lateral flow across the riparian zone. The amount sampled from each level of the riparian zone is defined by the lateral flow paths of the transmissivity feedback mechanism, which is consistent with an exponential increase in  $K_{sat}$  towards the soil surface

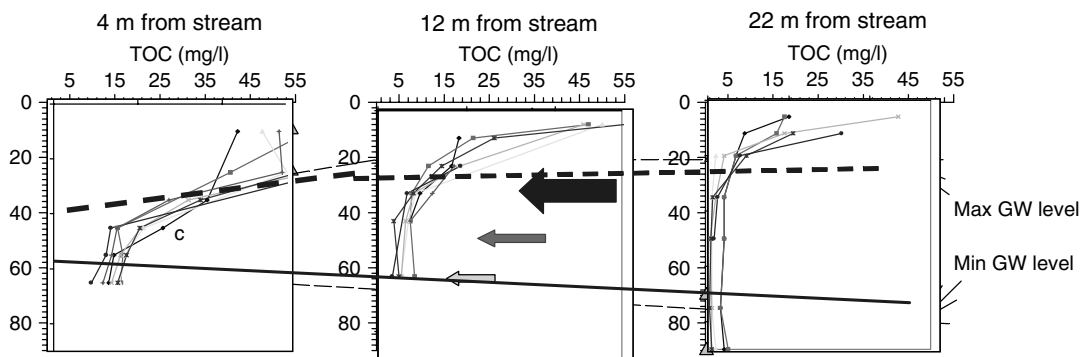


Figure 3. The DOC concentration on seven occasions during 1997 in a series of soil profiles along a hillslope transect at different distances from the stream. Note the high concentration of DOC in the superficial layer of the upslope sampling profile 22 m from the stream. This type of profile covers much of the catchment, but the hydrological connection of the DOC-rich mor layer to the stream goes via deeper mineral soils with low DOC concentrations. Thus, the mor layer is not a significant source of DOC to stream runoff on this catchment, even under most high-flow situations

The more conductive, superficial flowpaths ‘connect’ and transport ever greater amounts of lateral flow to the stream. This gives a mixture of proximal runoff sources dominated by the newly ‘connected’ superficial riparian soils with lower Ca concentrations. By the same token, the increase in DOC towards the soil surface in the riparian

soil profile gives an increase in DOC with flow. Cl, which has a constant concentration with depth (data not shown), is quite constant across the range of flow rates during spring flood (and other runoff episodes).

Mathematically, both the flow across soil profiles and the soil depth–soil solution concentration

relationships can be described as simple functions of depth. Integrating the product of flow and concentration in the riparian soils gives the predicted runoff chemistry (Figure 2). Stable tracers and many of the chemical constituents support this conceptualization. Thus, we believe we have an example that resolves the Double Paradox. The resolution builds on recurring patterns of flow at a scale of centimetres that are characteristic for different flow rates. These patterns define the connectedness of different catchment source areas to the stream, as well as within the catchment. The resolution is specific to this type of system, which, even though common in the boreal region, is at the simpler end of the catchment spectrum across which the Double Paradox has been observed.

## Discussion

The value of the resolution we propose lies on both the theoretical and practical planes. Theoretically, as long as the Double Paradox remains unresolved, there remains the possibility that it is not just nature's complexity, but lack of some basic process insight that is responsible for the failure to find a resolution. Such a possibility leaves catchment hydrology open to the speculation that it will always be an art of operational approximations rather than a quantitative science. Thus, even one example of resolving the Double Paradox is important for showing that there is not necessarily some fundamental gap in our understanding of catchment processes.

We think it is also important to remember the practical context from which the Double Paradox arose, namely the effort to understand how human perturbations affect water quality. This entails a synthesis of how biological, geochemical and hydrological processes interact to shape the quality and amount of runoff. Hydrology might have been seen as the 'simple' starting point for this interdisciplinary synthesis that could be called 'catchment science'. In the study of acidification, for example, which was one of the formative foci of catchment science, it quickly became apparent in the 1980s that hydrological knowledge was not up to the task of providing the 'plumbing' that defines the flow patterns linking complex biogeochemical processes within the catchment and

to the stream (Wheater *et al.*, 1986). As a result, catchment hydrology has been as much debated and questioned as any other part of catchment science.

Several innovative approaches have been found to use chemical information to try to help define catchment hydrology, e.g. end-member mixing analysis (Hooper *et al.*, 1990) and the interpretation of hysteresis (Evans and Davies, 1998). While such approaches have provided valuable insights into hydrology, these are also examples of where hydrology has not been as effective as it could have been in supporting other disciplines, since the chemical information has been used to build the hydrological interpretation rather than a better understanding of biogeochemical processes.

There is even a risk that the hydrological conceptualizations based on inferences from chemical patterns may be misleading. An example of this is the role of the forest floor mor layer (Figure 3) as a source of DOC in streams at high flow. The high DOC concentrations in the mor layer are obvious candidates for the source of elevated DOC at high flows, especially if a survey of potential catchment sources of DOC overlooked the few metre-wide swath of riparian zone soils. Hydro-metric data, though, conclusively demonstrate that the mor layer is not 'connected' hydrologically to the stream under many high-flow situations where DOC rises (Bishop *et al.*, 1993).

Drawing conclusions about flow pathways based on stream chemistry can thus lead to serious hydrological misconceptions. The only way to avoid such misconceptions is to have the hydrometric data needed to support the characterization of flow pathways. Simple systems, such as Nyänget, are important places to test our understanding of catchment hydrology. Here, hydrology can be defined well, and this helps us to learn more about specific biogeochemical processes. Improved process-level knowledge of both hydrology and biogeochemistry can then be used to constrain the conceptualizations of more complex systems. Resolving the Double Paradox is thus of importance for hydrology's role in supporting the other disciplines in catchment science and the resolution of specific environmental questions.

## Conclusions

What we have to offer as a resolution of the elegantly posed double paradox is not a commensurately elegant unified theory. But we do think it is a useful reminder of the value that basic field hydrology can have as a lever for gaining more information about the biogeochemical function of catchments. The more we know about hydrology, the more our research community can offer other disciplines in catchment science, and the effort to distinguish human influences from natural variation.

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