Using water age to explore hydrological processes in contrasting environments

While the spatial and temporal distribution of water resources is reshaped by changes in the underlying climatic drivers, the corresponding global demand for water is rapidly increasing. In this context, the chemical quality of surface water bodies represents an emerging issue for scientists, policy makers and managers. The chemical composition of river flows—and thus its suitability to satisfy certain human needs—reflects, in a dynamic manner, the spatiotemporal distribution of active water sources, and the relevant hydrological pathways connecting these potential sources to the catchment outlet. The concept of water age nicely encapsulates the hydrological history of the water stored in (some key compartments of) a catchment or released through its boundaries, providing quantitative information on how long water parcels belonging to a given storage or flux have been retained in the system (Kirchner et al., 2001; McGuire & McDonnell, 2006; Rinaldo et al., 2015). Early studies on use of age distributions in the context of transport models date back to more than 30 years ago (Cvetkovic & Dagan, 1994; Jury et al., 1986; Rinaldo & Marani, 1987). More recently, however, these early theories have been extended to incorporate the inherent dynamical nature of age distributions across different hydrological systems (Botter, 2012; Botter et al., 2010, 2011; Hrachowitz et al., 2013; van der Velde et al., 2012), highlighting the potential of general age conservation equations to describe a variety of environmental problems, from the characterization of discharge water quality to soil-vegetation dynamics and biogeochemical cycling (Benettin et al., 2017; Beyer et al., 2020; Birkel et al., 2011; Harman, 2015; Hrachowitz et al., 2016; Li et al., 2021; Rinaldo et al., 2015; Soulsby et al., 2015; Sprenger et al., 2019; Tetzlaff et al., 2014, 2021). The flexibility of this new theoretical apparatus, jointly with the availability of more extensive, cheaper and accurate analysis of tracers, has given rise to an increased number of studies where the concept of water age was used to characterize the chemical signature of streams, groundwater bodies and water taken up by vegetation. Nowadays, the quantification of water ages in different types of environmental systems represents one of the hottest topics in the hydrological literature, and applications of coupled flow and transport models are becoming widespread. Integrated models for water flow and solute transport, in fact, are able to provide a more accurate characterization of the relevant hydrological processes as compared to standard hydrological models (e.g., Beven & Davies, 2015; Hrachowitz et al., 2015; Kuppel et al., 2018; Wilusz et al., 2020). This reflects the intertwined coupling between water quality and quantity in river systems, which calls for the development of comprehensive and integrated modelling tools, as mirrored by the observed increase in the number of studies on the characterization of the ages in the critical zone, where such coupling is particularly evident.

This Special Issue of Hydrological Processes provides a collection of contributions that exploit the concept of water age and focus on challenges and opportunities provided by different environments in terms of data availability, processes identification, interpretation of measurements and models. The Special Issue combines theoretical and empirical work that explore synergies among data, models and process interpretation under a variety of climatic and geographic settings. In particular, the papers belonging to this Special Issue can be grouped into five main thematic areas: (i) theoretical investigations about the structure of water ages in river basins and hillslopes; (ii) papers exploring water ages in different snow-impacted catchments ranging from North-America to Europe; (iii) the characterization of water age distributions in seasonally low-rainfall and drought settings; (iv) water age studies in Australia, with specific reference to some of the wettest regions of this relatively dry continent. A miscellany of papers from other regions of the World (from the Tropics to the Tibetan region) nicely complements this Special Issue. The latter contributions involve a set of catchments which share the common feature of being ‘unique’ in terms of catchment features or investigated processes. These sets of topics covered by the Special Issue are summarized in the following sections.

1 | THEORETICAL ANALYSES

The studies by Rodriguez et al. (2020), Zarlenga and Fiori (2020) and Rigon and Bancheri (2021) provide nice theoretical advances in the characterization of water age distributions in rivers, and analyse the linkages between water ages, catchment structure and climatic forcing. In particular, Rodriguez et al. (2020) explore the origin and the implications of multimodal age distributions of catchment-scale discharge. The analysis reveals that multimodal age distributions are
likely to occur in the outflow of complex watersheds forced by unsteady climate, particularly in the presence of heterogeneous flowpaths and/or water velocities. However, this key signature of the age structure of the streamflow might not be clearly detectable from a single tracer concentration timeseries at the outlet, thereby highlighting the importance of multi-tracer studies. Zarlenga and Fiori (2020), instead, present a physically-based framework for the analysis of water and solute age distributions in hillslopes. The analysis is based on the Boussinesq approximation of the full three-dimensional flow and age equations under transient conditions, and provides a set of novel expressions for the moments of the water age along a control plane perpendicular to the mean flow. The study shows that the unsteady nature of rainfall and climate is the primary driver of water ages in hillslopes, while the relationship between the age structure of the storage and that of the outflow depends on key topographic properties such as the bedrock slope and the hillslope shape. The relationship between age distributions of different components of a complex hydrological system is also the subject of the work contributed by Rigon and Bancheri (2021), in which the relationships among the internal structure of a complex hydrological systems and the ensuing age/response time distributions are studied starting from simple water budget equations which encapsulate the underlying catchment structure. The paper offers a framework to couple flow and transport models in a coherent manner, combining analytical results and a set of practical examples.

2 | WATER AGES IN SNOW IMPACTED CATCHMENTS

The papers by Campbell et al. (2020), Ceperley et al. (2020), Cooke and Buttle (2020) and Leach et al. (2020) analyse the structure of water ages in catchments which experience—to a quite heterogeneous extent—significant snow dynamics. The geographical coverage of this group of papers ranges from North America (Ontario and Alberta) to Italy and Switzerland. Ceperley et al. (2020) showed that seasonal snow cover leads to small young water fractions (i.e., ages younger than 2–3 months) and a significant dampening in the discharge isotopic signature. The study also highlights important methodological issues associated with the reconstruction of isotopic precipitation signal from sparse samples, and emphasizes how glacier-dominated catchments are characterized by larger young water fractions as compared to snow-dominated settings. The limited contribution of young water ages to the discharge observed at the outlet of snow dominated catchments also emerges from the study of Campbell et al. (2020), who analysed with the aid of numerical simulations the applicability to snow-dominated settings of methods based on the equivalence between young water fractions and isotope amplitude ratios (Kirchner, 2016a, 2016b). The papers by Cooke and Buttle (2020) and Leach et al. (2020), instead, are focused on the analysis of the intra-regional variability of age-related signatures in central and southern Ontario (Canada). The authors evidence important spatial heterogeneity in mean discharge water ages and young water fractions, depending on catchment characteristics (e.g., flowpath length, land-use/land-cover) and key hydrologic indexes (such as the baseflow index and discharge variability), discussing the important implications in terms of stream water quality and catchment storage potential. Overall, these studies provide more insight on the relationship between snow dynamics and water ages across different geographic regions, but also indicate that caution should be used in applying standard tools for the analysis of the structure of water ages to snow dominated contexts, where heterogeneity in elevation, geology, topography and climate could play a key role in shaping the hydrochemical response of rivers.

3 | WATER AGES IN SEASONALLY DRY CATCHMENTS

Most early investigations of water age tended to be based in more humid environments and in relatively undisturbed experimental catchments where the impact of human activity was relatively unobtrusive. This tended to: (a) underplay the importance of evapotranspiration (or ‘green water’) fluxes in affecting the ages of residual groundwater recharge and stream flow (of ‘blue water’) fluxes and (b) ignore the role of anthropogenic influences on water ages in ‘real world’. The paper by Grande et al. (2020) addresses both of these issues focusing on a small catchment in California, USA, which experiences a Mediterranean climate and drains a rural mountainous headwater but passes through a downstream urban area. Using a combination of isotopic and geochemical tracers, they showed that stream flow was considerably younger than groundwater stored in the catchment (~1 year compared with ~10 years respectively) reflecting the seasonal influence of the wet period and relatively young water on stream flow generation. Interestingly, the authors also show that irrigation water from a golf course, whilst only a minor component of the annual water balance, formed a significant fraction of stream flow. Gallart et al. (2020) also report results of isotopic studies from a Mediterranean climate in the Vallcebre research catchments, Catalonia, Spain. Strong hydroclimatic seasonality restricts the wettest periods to autumn and spring, with both summer and winter being dry. However, the mountainous catchment is dominated by clay rich bedrock. Consequently, climate and geology combine in wet periods to produce an extremely ‘flashy’ hydrological response. They highlight the importance of high resolution isotope sampling in this environment to accurately characterize the age distribution of younger water in stream flows, and show how routine weekly sampling typical of many monitoring programmes may lead to serious underestimation of young water fractions. In contrast, Smith et al. (2020) focus on plot scale studies in a lowland catchment in Germany in the early stages of recovery from the 2018 drought that affected much of Europe. They use isotope data collected under contrasting co-dominant land uses of forests on more sandy soils and grassland on more loamy soils. The data was used in calibration of the tracer-aided, process-based ecohydrological model ECh2O-iso
(Kuppel et al., 2018) to estimate effects of land use on water partitioning and water ages in order to assess implications for drought recovery. Evapotranspiration is higher under forest, leading to drier soils, higher soil water ages and longer recovery times for soil moisture stores to replenish. This also leads to older recharge waters under forests, and older transpiration ages as trees can access deeper, older water. Such process-based modelling of age evolution in the critical zone of soil-vegetation units can also provide the basis for understanding implications for drought recovery at the catchment scale (Smith et al., 2021).

4 | WATER AGES IN SEASONALLY WET CATCHMENTS IN AUSTRALIA

Some of the earliest work on estimating stream flow ages was based in Australia (Turner et al., 1987), a country where the combination of dry conditions or marked hydroclimatic seasonality, combines with a complex, ancient geological settings poses distinct conceptual challenges to water age studies. These are compounded by logistical challenges of sampling in often large, remote catchments. Cartwright et al. (2020) used tritium dating of streamflow in a number of mesoscale catchments in Victoria to ascertain Mean Transit Times of base flows and to relate these to potential climatic and landscape controls. However, identifying such linkages proved much more difficult than in some other geographical regions, probably because of the influence of large, but poorly constrained groundwater stores in deep weathered zones sustaining baseflows, resulting in very old (upto 100 years) water ages. In addition, very high evapotranspiration rates limited young water influences to wetter periods when near surface flow paths are well connected. Identifying these complexities of controls underlines how different age characteristics can vary in contrasting geographic and hydroclimatic environments and highlights the dangers of assuming landscape (e.g., topography, soils, etc.) controls are transferable. Buzacott et al. (2020) also found that high evapotranspiration and deep groundwater sources (this time in fractured bedrock aquifers) had a strong influence on the Corin catchment in the Australian Alps. They used time series of stable isotope data in precipitation and streamflow to identify storage selection (SAS) functions to estimate the ages of streamflow, catchment storage, and evapotranspiration. Whilst evapotranspiration was found to show a strong preference from relatively young water (~2 years old), streamflow was well-mixed, with ages relatively stable (~5 years) and showed only a weak preference for younger water and older waters when the catchment was wet or dry. However, uncertainty was large and the size of the groundwater store poorly constrained due to the limitations of stable water isotopes in capturing ages of more than a few years. Moreover, the stream water data was limited to a year of sampling. Nevertheless, the study, which is the probably the first application of the SAS methodology in Australia, showed the strong influence of evapotranspiration on stream water ages and identified the importance of large groundwater storage. This demonstrated the utility of the SAS approach in data sparse catchments.

5 | MISCELLANEOUS PAPERS

The last group of papers exemplify the diversity of approaches that are available to assess water ages under different climates and using different type of tracers. The hydrological systems investigated in this group include: an agricultural catchment in France (Benettin et al., 2020), the aquifer of a forested catchment in Sweden (Kolbe et al., 2020), two sites in the tropics, where one is a hillslope of volcanic ash soil (Mosquera et al., 2020) and the other is a rainforest catchment (Correa et al., 2020) and two sites in China, where one is a Karst catchment (Zhang et al., 2020) and the other is a large, high-elevation river basin (Yang et al., 2021). Water age is used by Benettin et al. (2020) to explain catchment-scale removal of agricultural nitrate. They find that, while nitrate removal likely occurs throughout the year, its effect is only visible at very low flows before the winter, when streamflow is mainly sustained by deeper and older groundwater. The age analysis, based on tracer data (chloride), focused on the younger (<1 year) water components. This is typical in catchment hydrology but it is different from groundwater approaches, which tend to focus on a different—and older part of the age distributions. Indeed, Kolbe et al. (2020) computed groundwater age based on the Boussinesq model and CFC data from nine wells and found mean groundwater ages of 20–80 years. Age stratification showed a quick increase to 30 years just below the water table which was explained by return flow of groundwater in the surface discharge zone. Water age stratification is also addressed by Mosquera et al. (2020), with different tools and tracers. They measured water stable isotopes at 2-week interval over 3 years along a soil hillslope transect in Ecuador, in the tropics. Mean water age, computed trough the standard convolution integral, suggests that vertical flow paths dominate the system and generate a mean water age stratification from about 2 weeks in the top 10 cm to about 9 months at 65 cm depth. The other study based on the tropics (Correa et al., 2020) was largely influenced by vegetation uptake ad transpiration. Therein, water ages were computed through a conceptual, spatially-explicit model run at high spatiotemporal resolution and calibrated against water flow and stable isotope data. Mean streamflow age was estimated to range from just a few hours to a few years depending on the hydrologic conditions. The high spatiotemporal resolution of the model further allows the authors to explore how vegetation and topography affect water fluxes and their age in both time and space. Work by Zhang et al. (2021) is a relatively rare example of catchment water age study influenced by a karst system. Water age was evaluated through a lumped transport model calibrated on stable isotope data and it was compared with the (mean) young water fraction estimated through tracer cycle damping. The share of young water in streamflow appears to be driven by storage variability and by connectivity between the conduit network and the stream. Because of this connectivity, young water was estimated to contribute almost entirely to streamflow right after a storm event, with implications for the quick transport of contaminants. Finally, Yang et al. (2021) worked on three sub-basins of about 5000 km² each and identified the need for age indicators that quantify not just the fraction of young water but also the fractions of water younger/
older than 1 year. They proposed a preliminary methodology based on the annual water balance to compute such fractions and found that
on average the fraction of water younger than 1 year, and thus
affected by just 1 cycle of thawing/freezing, was about 80%.

The Special Issue demonstrates the incredible diversity of
instances in which the concept of water age proves to be useful for
interpreting hydrologic dataset and investigating the underlying driving
processes. The generality of the formulation, which often capitalizes
on age mass balances formulated within suitable domains, makes it a
useful tool applicable to a variety of settings, as demonstrated by the
large diversity of climates, hydrologic systems and methods embraced
by this Special Issue. Most of the studies included here makes use of
the concept of young water fraction (evaluated either from models cal-
ibrated on tracer data or directly from tracer cycle damping). This
shows that the community is progressively moving away from ‘tradi-
tional’ concepts originally conceived under stationary conditions to
more sophisticated age metrics capable of better representing the
complexity of age structures in dynamic environmental systems.

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