3.4 Way forward towards a transferable qualitative tracer and towards quantitative approach

As exposed in sections 3.2 and 3.3, TTI is a new tool which seems to have a real potential to be a qualitative natural tracer of transit time. To make TTi a quantitative natural tracer of transit time, several avenues have to be explored, such as artificial tracer test, use of radiogenic isotopes, or the study of organic matter degradation kinetics.

Artificial tracer test consists in injecting a tracer in a place known for its strong and rapid connectivity with the hydrosystem, and in monitoring its restitution at a presumed outlet. It thus informs about the existence of a path between the injection point and the outlet, and provides an estimate of the transit time between the two. A set of several artificial tracer tests may provide enough transit time values to quantitatively connect TTi with transit time. However, to compare TTi with artificial tracer tests it is necessary to check that they provide the same information. An artificial tracer test with uranine, tryptophan and humic-like organic matter performed by Frank et al. (2020) in a karst system shows that uranine has the same transport properties as tryptophan but not as humic-like organic matter. It therefore seems that artificial tracer tests may not correctly illustrate the behaviour of all the organic matter compounds involved in TTi. Moreover, not all artificial tracers may be compatible with simultaneous analysis of natural fluorescence of organic matter. For example, widely-used uranine may overlay the natural fluorescence of protein-like compounds (P1, Tyrosine-like). Indeed, the quantification of artificial tracers in a sample is performed by spectrofluorescence, exactly like the quantification of fluorescent organic matter compounds needed to calculate TTi. Some artificial tracers have emission and excitation wavelengths in the same area of the EEM of some organic compounds, and may thus hide the natural signal of organic matter. Use of such tracers would not be compatible with quantification of TTi. Furthermore, some organic matter compounds have the ability to adsorb themselves to artificial tracers molecules, which would interfere with the TTi signal. Selection of an artificial tracer in such an experiment will therefore have to be taken with caution. A more fundamental remark is that TTi is related to residence time of a mix of water originating from different paths within the aquifer, while artificial tracers only trace the fastest circulations due to injection through well-connected conduits. This observation raises the question of the comparability of transit time evidenced by both methods. In addition, the presence of possible injection points is not guaranteed for all hydrosystems. For example, no possible injection point could be identified at Millet spring for now. As a conclusion, artificial tracage may be a good candidate to identify fast infiltration, as long as no interference is possible (fluorescein usage), and obtain transit time is not mistaken for residence time.

A second approach to establish a quantitative link between TTi and residence time is the use of radiogenic isotopes like beryllium-7, radium or radon-222 (Frey et al., 2011; Molina-Porras et al., 2017). Price taken apart, the use of radiogenic isotopes may be problematic because of the volume of water needed for analysis which reaches several hundred of litters (e.g 500 L for Beryllium-7, Frey et al., 2011) which reserves its use for water flow points with sufficient discharge for sampling to be performed within a sensible time scale. The sampling time for radiogenic isotopes from some flow points in our study can be several days. Even quite important springs may reach low discharges that prevent such analysis during low flows. Nevertheless, radiogenic isotopes can be relevant for linking TTi to transit time values for samples from springs and flows having a sufficient discharge.

The study of the degradation rate of organic matter is also necessary to transform TTi as a quantitative natural tracer because it may help to estimate the duration life of each kind of organic matter in the natural environment, and therefore inform on transit time. In soil, the biodegradation of labile organic matter was estimated from 2 to 5 days while the stable organic matter ranges from 0.2 to 8.6 years (half-life from Kalbitz et al., 2003). But the biological activity is more important in soils than in groundwaters. Therefore, these lifetimes obtained in soils are probably shorter than those in groundwaters. A recent paper based on the improvement of dissolved organic matter degradation understanding in groundwater pointed out the lack of knowledge on this subject (McDonough et al., 2022). As little is known about the behavior of DOM in natural waters, even less is known about fluorescent organic matter, which is a small part of the DOM. The paper cited previously therefore discusses very long transit time (several years) while we are considering very short ones (weeks to months). Nevertheless, interesting studies were performed about fluorescent organic matter degradation kinetics in soils, or in wastewater, testing different water treatment (De Willigen et al., 2008; Conant et al., 2011; Choi et al., 2017; Guo et al., 2020). These studies are heavy to perform, but they could be adapted to natural water in order to improve fluorescent organic matter natural degradation and therefore helps to TTi development.

Transferability of TTi in different pedoclimatic and anthropogenic contexts may also be questioned. Indeed, anthropic activities and seasonality may affect TTi through organic matter production and degradation :

- Fluorescent organic matter is mainly coming from vegetation related to plant cycle. As the vegetation changes with the seasons, the organic matter supply changes as well, at least in terms of quantity. Seasonality does not significantly affect organic matter composition, as exposed in Musadji et al. (2019). Anthropic activities such as land use or wastewater infiltration within the hydrosystem can affect both quantity and types of organic matter compounds because they involve input of external organic matter to the system. The influence of anthropic activity on the type of organic matter compounds may be significant and may vary over time. Moreover, the anthropic activities and the vegetation may vary from one site to another due to different pedo-climatic conditions and complicate the transposition of a quantitative TTi.

  As TTi is a ratio of different organic matter compounds, it is made independent from the absolute amount of organic matter. Possible bias may appear when very low input of a specific type of organic matter results in DOM content below the detection limits. In this case, degradation is overestimated which may impact the quantitative relation between TTi and transit time. Overall, we expect TTi to be little affected by seasonal variations of productivity even if it is quantitatively linked to residence times. As TTi is a ratio, a regular and constant supply of anthropic organic matter may not impact its variation. But in contrast, a punctual supply of humic or protein-like organic matter may result in an over or underestimation of TTi.
- The degradation of organic matter involves interactions with biocenose. Degradation occurs at different rates depending on the type of organic matter compounds and on the biodiversity and microbial activity of the soil. The latter may vary throughout seasons and with anthropic activities because of varying factors such as sunlight duration, moisture rate, temperature, climate or pesticides use.

Variation in space and time in organic matter composition and degradation rate may thus stem from either anthropic or natural factors. Influence of anthropic compounds can be circumvented by careful identification and separation of PARAFAC components. Variation in organic matter composition and degradation kinetics in different pedoclimatic contexts is not an obstacle to the qualitative use of TTi, but may be a serious limitation to the transferability of a quantitative link between TTi and residence time. Variation in organic matter degradation kinetics with time on the same hydrosystem throughout the year is questionable but it begins to be studied as shown by McDonough et al. (2022). A detailed study of composition of organic matter source in soil and of its becoming in groundwater through lab tests may provide valuable elements to estimate the lifetime of fluorescent compounds in hydrosystems, and thus to quantitatively link TTi with transit time.

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