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Variability of pesticides and nitrates concentrations along a river transect: chemical and isotopic evidence of groundwater – surface water interconnections

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Groundwater quality is increasingly monitored in Europe where various levels of nitrate and pesticide and/or metabolite contamination have been demonstrated (Loos et al., 2010, Stuart et al., 2012). The Groundwater Daughter Directive (2006/118/EC) to Water Framework Directive (WFD) particularly requires measures to prevent or limit inputs of pollutants into groundwater and compliance with good chemical status criteria (based on EU standards of nitrate and pesticides). The WFD mentioned the need to protect groundwater but also to have a particular regard to its impact and interrelationship with associated surface waters and directly dependent terrestrial Ecosystems.

The Ariège river basin (SW France $-538~\rm km^2$) is an alluvial plain under high agricultural pressure leading to a contamination of the aquifer by several pesticides and metabolites (Amalric et al., 2013). The Crieu is an allochtone river, crossing the plain ($\sim 10~\rm km$ length) before joining the Ariège River. The Crieu is often dry in its middle section suggesting water leakage from surface water towards groundwater. At the opposite, the permanent flow observed downstream suggests an input of groundwater into surface water. In May 2014, while the Crieu flow was continuous through the plain, 7 river samples were collected and analyzed for pesticides, major ions, strontium concentration and isotopes. In situ measurements of electric conductivity were also performed as well as flow gauging. Two groundwaters close to the river were also sampled.

The flow gauging measurements show a decreasing river discharge in the central area of the Crieu River, suggesting surface water leakage towards groundwater. Nevertheless, the electric conductivity increases along the river flow as well as some pesticides and nitrates concentrations. This chemical evolution of the river water is thus inconsistent with a simple water infiltration and another source of dissolved solutes is required to explain the increased of concentration. Finally, downstream the quantified pesticides were different from those observed in the upper part of the Crieu but similar to those observed in groundwater.

Sr isotopes together with major elements and Sr concentrations allow to identify 3 distinct end-members to explain the river quality evolution: 1) surface water, 2) groundwater and 3) sub-surface water. On this basis, we first demonstrate that the contribution of the different end-members to the river flow is highly variable from upstream to downstream. Secondly, we evidence water exchanges between the river and the groundwater compartment and vice-versa.

The combination of the isotopic and geochemical approaches was essential to understand the complex relations and exchanges between surface and ground-waters occurring in few kilometers along the Crieu River. This understanding allows the comprehension of spatial variability of surface water quality. This is of primary importance when to help water managers to select relevant sampling points to be monitored in the framework of the WFD.

Amalric L., et al. (2013). International Journal of Environmental Analytical Chemistry, 93: 1660-1675 Loos R. et al. (2010). Water Research, 44: 4115-4126 Stuart M. et al. (2012). Science of the Total Environment, 416: 1-21.