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Understanding the Origins of Pesticides Metabolites in Natural Waters through the Land Use, Hydroclimatic Conditions and Water Quality

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Abstract: Brittany (France) is an agricultural region, where emerging pollutants are highly at risk to reach water bodies. Among them, pesticides metabolites are frequently detected in surface waters. The Vilaine watershed (11 000 km²) is of great interest, as a large drinking water treatment plant (100 000 m³/day) is located at the extreme downstream of it. This study aims to provide an evaluation of the pesticides metabolites pollution in the Vilaine watershed, and an understanding of their availability, in order to protect the water resource. Hydroclimatic conditions, land use, and water quality parameters controlling metabolites availability are emphasized. Later this knowledge will be used to understand the favoring conditions resulting in metabolites export towards surface water. 19 sampling points have been strategically chosen along the 220 km of the Vilaine river and its 3 main influents. Furthermore, the intakes of two drinking water plants have been sampled, one is located at the extreme downstream of the Vilaine river and the other is the riparian groundwater under the Vilaine river. 5 sampling campaigns with various hydroclimatic conditions have been carried out. Water quality parameters and hydroclimatic conditions have been measured. 15 environmentally relevant pesticides and metabolites have been analyzed. Also, these compounds are recalcitrant to classic water treatment that is why they have been selected. An evaluation of the watershed contamination has been done in 2016-2017. First observations showed that aminomethylphosphonic acid (AMPA) and metolachlor ethanesulfonic acid (MESA) are the most detected compounds in surface waters samples with 100 % and 98 % frequency of detection respectively. They are the main pollutants of the watershed regardless of the hydroclimatic conditions. AMPA concentration in the river strongly increases downstream of Rennes agglomeration (220k inhabitants) and reaches a maximum of 2.3 µg/l in low waters conditions. Groundwater contains mainly MESA, Diuron and metazachlor ESA at concentrations close to limits of quantification (LOQ) (0.02 µg/L). Metolachlor, metazachlor and alachlor due to their fast degradation in soils were found in small amounts (LOQ - 0.2 μg/L). Conversely glyphosate was regularly found during warm and sunny periods up to 0.6 µg/L. Soil uses (agricultural cultures types, urban areas, forests, wastewater treatment plants implementation), water quality parameters, and hydroclimatic conditions have been correlated to pesticides and metabolites concentration in waters. Statistical treatments showed that chloroacetamides metabolites and AMPA behave differently regardless of the hydroclimatic conditions. Chloroacetamides are correlated to each other, to agricultural areas and to typical agricultural tracers as nitrates. They are present in waters the whole year, especially during rainy periods, suggesting important stocks in soils. Also Chloroacetamides are negatively correlated with AMPA, the different forms of phosphorus, and organic matter. AMPA is ubiquitous but strongly correlated with urban areas despite the recent French regulation, restricting glyphosate to agricultural and private uses. This work helps to predict and understand metabolites present in the water resource used to craft drinking water. As the studied metabolites are difficult to remove, this project will be completed by a water treatment part.

Keywords: agricultural watershed, AMPA, metolachlor-ESA, water resource **Conference Title:** ICPC 2018: International Conference on Pesticide Chemistry

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