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Long-term monitoring of plant protection products and their transformation products at karstic springs

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Karst aquifers are an important water resource for a large part of the world's population. Because of their natural susceptibility towards contamination, they have to be managed carefully. Human activities such as agriculture, roads or settlements in karst aquifer catchments often lead to the contamination of karstic springs. Due to their special geology, they are at risk of both, long- and short-term contamination. Long-term contamination is due to adsorption of anthropogenic substances in the overlaying soil, the epikarst or rock matrix whereas short-term contamination can be due to spills or precipitation events. Such precipitation events can lead to the mobilization of substances. These are then readily transported to karstic springs where pollutant peaks might be observed. However, current monitoring strategies are not suitable (infrequent, regular sampling intervals) to reveal such peaks. The goal of this study was in a first step, to investigate the contamination level of ten karstic springs (part of NAQUA Swiss National Groundwater Monitoring) in the Swiss Jura, screening for plant protection products (PPP) and transformation products (TP). This was achieved by a monitoring campaign that was conducted from March 2020 until October 2020. Two-week composite samples were collected in addition to the continuous acquisition of electrical conductivity and water level, i.e. spring discharge. Samples were then analyzed by large volume direct injection into a HPLC-HRMS/MS setup using a target list of 130 compounds (105 PPP's, 25 TP's).

Analysis of a first batch of samples of three springs did not reveal many compounds with elevated concentrations (33 detections in 15 samples above 100 ng/L of 3 compounds: chloridazone desphenyl, chloridazone methyl desphenyl, chlorothalonil TP R471811). No PPP's were observed to be continuously leaching from the catchment and the aquifer in concentrations above 100 ng/L. The detected compounds above 100 ng/L were TP's which indicates that their parent compounds might be adsorbed to the aquifer matrix or the soil cover, therefore leaching TP's continuously or pulse like during rain events. In total, 19 compounds were detected above their quantification limits. Of those, 10 PPP's and 9 TP's were found. We further evaluated spring responses during rain events based on electrical conductivity and determined response times between 3 and 5.5 hours. Since two-week composite samples cannot reveal short-term concentration dynamics given the fast response times and dilution (both leading to low concentrations in composite samples), we will conduct a sampling campaign with a different strategy in 2021. Therein, in a second step,

the goal is to study the pollutant dynamics induced by precipitation events with temporally highly resolved measurements. To achieve this we will install a transportable, liquid chromatography, high resolution mass spectrometer at three selected springs and conduct an automatic sampling and analysis with a high temporal resolution.