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

Johannes Schorr[1,2], Franziska Jud[1], Birgit Beck[1], Philipp Longree[1], Heinz Singer[1], Juliane Hollender[1,2]

HS2.3.3 EGU21, Display Material

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The Why?

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- Current monitoring strategies (1-4 grab samples per year) are **not suitable** to cover pollutant dynamics in karstic springs which tend to react fast during/after precipitation events
- Many springs are used as **drinking water resources**
- Important **pollutant peaks** might be **missed**, yet they influence drinking water quality

Goals of the monitoring campaign

Johannes Schorr[1,2], Franziska Jud[1], Birgit Beck[1], Philipp Longree[1], Heinz Singer[1], Juliane Hollender[1,2]

Explorative character:

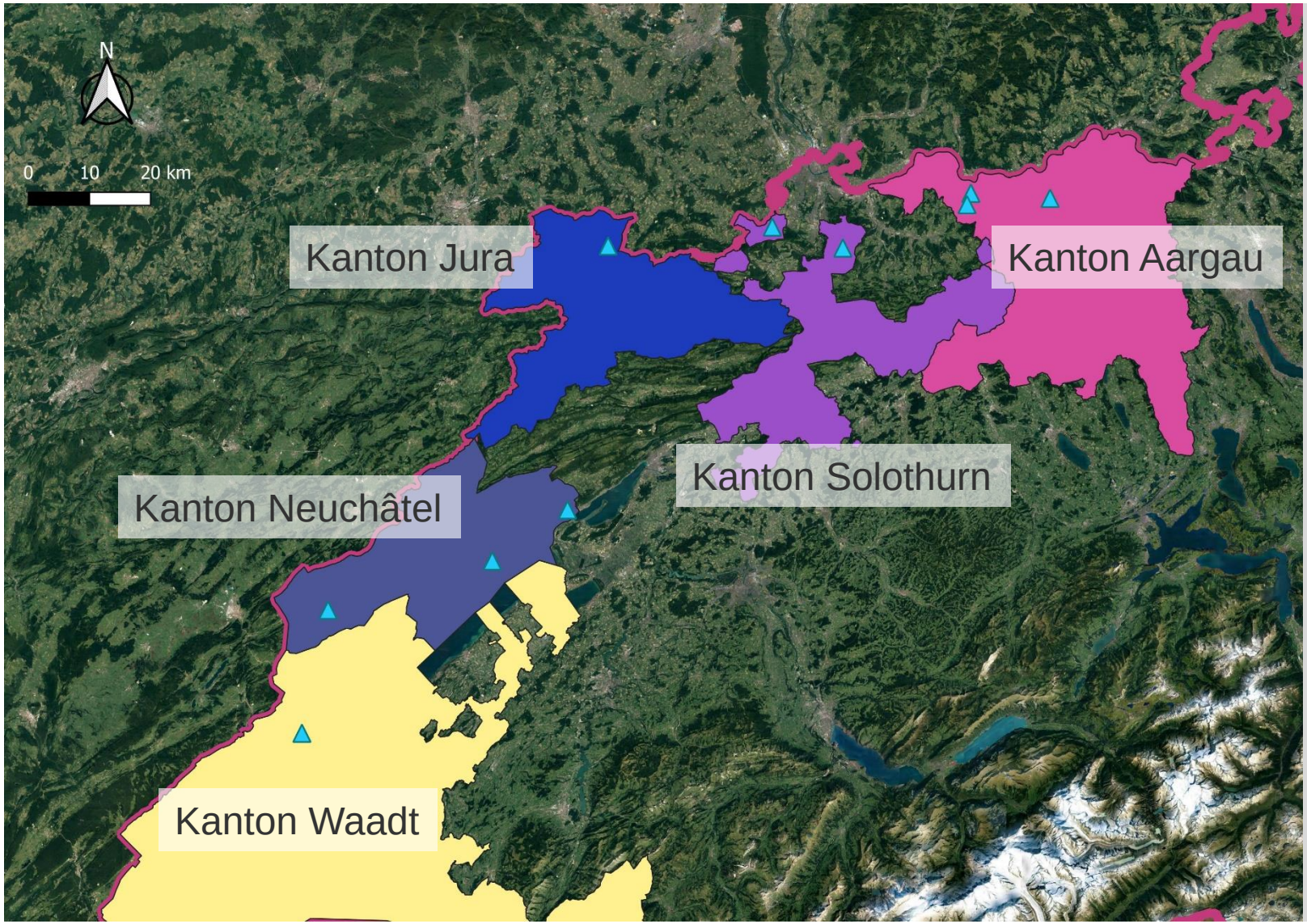
- Establish an **overview** of the overall scale of plant protection product (**PPP**) and their transformation products (**TP**) pollution in **10 karstic springs**
- Study the **longterm dynamics** of pollutants in the application period
- Explore **hydrogeology** of karst aquifers

→ **Find 3 most interesting* springs to study high-frequently with a transportable online MS (MS^2field)**

*Interesting: i.e. high concentrations, quick response of the springs to rain events, high agricultural activity in catchment

Methodology

Johannes Schorr[1,2], Franziska Jud[1], Birgit Beck[1], Philipp Longree[1], Heinz Singer[1], Juliane Hollender[1,2]



- **2-week composite samples** at **10 study sites** throughout the Swiss Jura during application period of pesticides 2020
- Analysis of 130 target compounds with **RPLC-HRMS/MS** and **IC-HRMS/MS** (including urban water indicators and nitrate)
- **Hydrological parameters:** electrical conductivity, turbidity, temperature, pH, discharge

Results – Overall contaminant load

Johannes Schorr[1,2], Franziska Jud[1], Birgit Beck[1], Philipp Longree[1], Heinz Singer[1], Juliane Hollender[1,2]

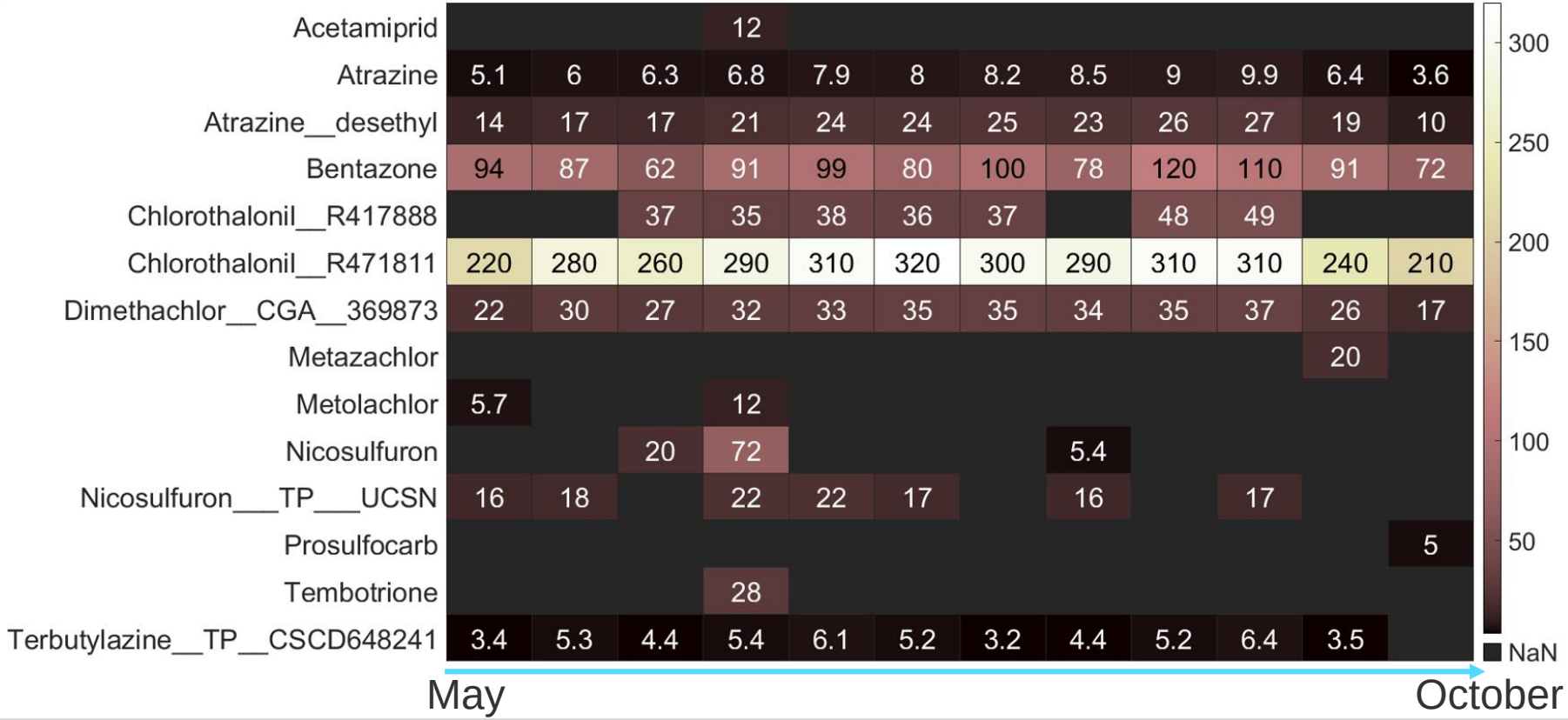
Spring	# of detects >LOQ (2020, 130 compounds)	Average concentration sum (2020, ng/L)	Agriculture in catchment (%)
1	9	1109	69
2	5	7	6
3	15	661	43
4	3	10	19
5	9	52	14
6	1	5	0
7	7	289	50
8	14	480	58
9	5	58	6
10	9	214	19

Chosen for an intensive sampling campaign (2021-2022) with the MS2field

- High temporal resolution
- Sensitive method (large volume direct injection)
- High resolution mass spectrometry

Results – Example spring 8

Johannes Schorr[1,2], Franziska Jud[1], Birgit Beck[1], Philipp Longree[1], Heinz Singer[1], Juliane Hollender[1,2]



- Rather constant concentrations: Atrazine, atrazine-desphenyl, bentazone, chlorothalonil R471888, dimethachlor CGA369873, terbutylazine TP CSCD648241
- Sporadic occurrences of a few other compounds

Results – Example spring 8

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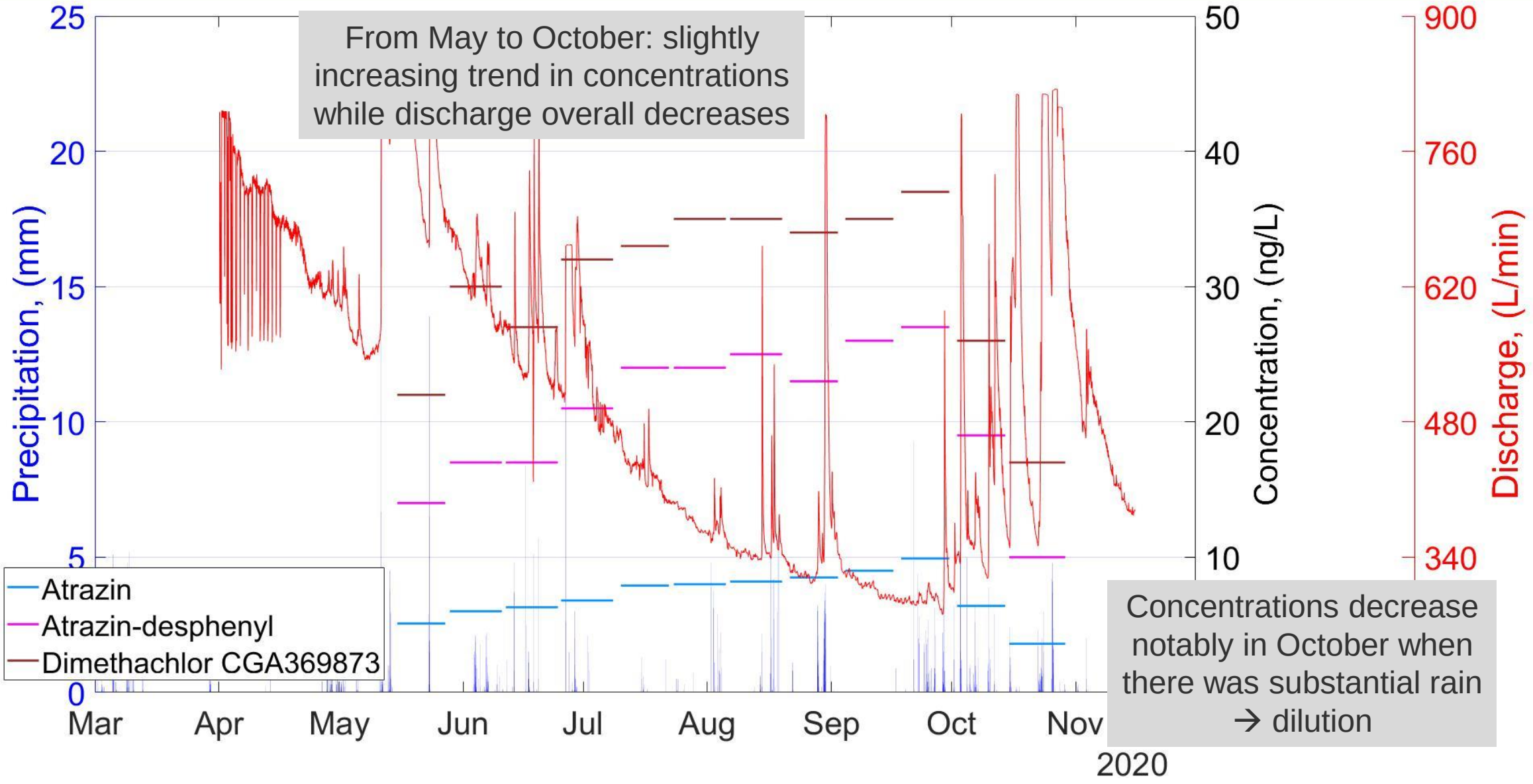


Conclusions (1)

Johannes Schorr[1,2], Franziska Jud[1], Birgit Beck[1], Philipp Longree[1], Heinz Singer[1], Juliane Hollender[1,2]

Springs 1, 3 and 8:

- are contaminated the most, !
- have the highest portion of agriculture in their catchments and
- react reasonably fast to precipitation events ·····▸

2-week composite samples are suitable to monitor the overall pollutant picture to answer the questions:

- Which pollutants are continuously present in which concentrations at the respective springs?
- How is their temporal pattern during the application period?

Conclusions (2)

Johannes Schorr[1,2], Franziska Jud[1], Birgit Beck[1], Philipp Longree[1], Heinz Singer[1], Juliane Hollender[1,2]

However, 2-week composite samples are likely <u>not</u> suitable to:

- capture fast temporal dynamics of pollutants in karstic springs
- and detect all PPP's that occur only in very short time periods after their application

→ The interplay of actual presence of PPP's and precipitation makes it hard to detect them with periodic monitoring strategies (e.g. infrequent grab sampling). Peak concentrations potentially exceeding drinking water limits likely remain undetected.

Outlook – Goals of the PhD-project

Johannes Schorr[1,2], Franziska Jud[1], Birgit Beck[1], Philipp Longree[1], Heinz Singer[1], Juliane Hollender[1,2]

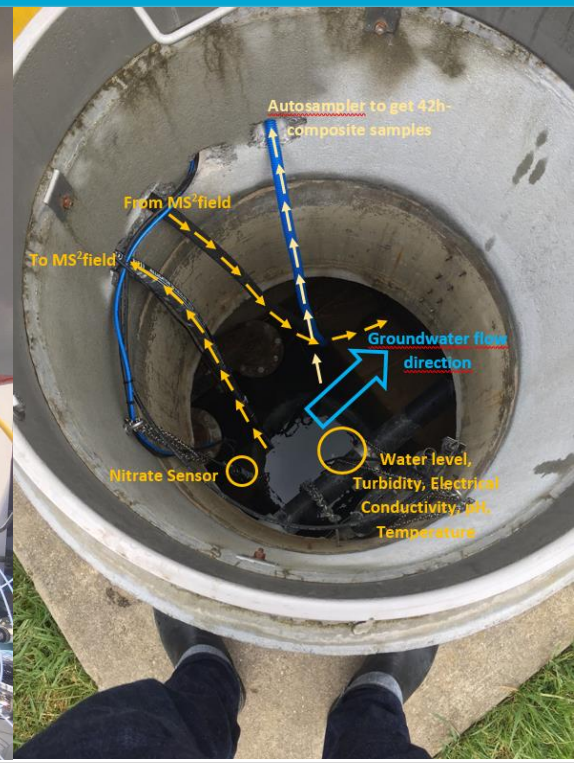
- Gain insights into the dynamics and the scale of **PPP contamination** in karstic springs

  → Detect peak events of PPP's, PPP-transformation products in karstic springs with a highly sensitive online approach using the MS^2field

- Propose a re-evaluation of current monitoring strategies of karstic springs and eventually agricultural practices in agriculturally influenced catchments

Outlook – Project status

Johannes Schorr[1,2], Franziska Jud[1], Birgit Beck[1], Philipp Longree[1], Heinz Singer[1], Juliane Hollender[1,2]



- Since March 2021: Sampling with the MS2field at three selected springs throughout Swiss Jura
- Online in-situ analysis (MS²field) of:
  - 150+ PPP's and their TP's; nitrate; electrical conductivity; turbidity, pH, temperature, discharge, precipitation
  - Bacterial cell concentration (online flow cytometry)
- In addition to: 42-hour composite samples, event-based grab-samples