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INSPIRATION bulletin

CL:AIRE's INSPIRATION bulletins describe practical aspects of research which have direct application to the management of contaminated soil or groundwater in an agricultural context. This bulletin describes the use of micropollutants to investigate anthropogenic impacts to a watershed.

Micropollutants as tracers for anthropogenic impacts on groundwater quality and recharge sources on a local scale – the case study of Fehraltorf, Switzerland

1. Introduction

Groundwater recharge is an important factor to characterise in efforts to manage the quantity and quality of water resources and to ensure healthy ecosystem function. In most environments, characterisation of groundwater cannot be properly carried out by assessing natural controls only. The widespread development of the landscape by humans often has a profound impact on the characteristics of groundwater recharge, flow pathways and quality (Blanchoud *et al*., 2007; Jurado *et al*., 2012; K'oreje *et al*., 2016). These influences have proven to be a challenge to characterise. While many case studies to this end exist (e.g. Dimitriou and Moussoulis, 2011; Sheikhy Narany *et al*., 2017), to date there is no generalised formulation of the relationship between land use change and groundwater response.

Many methods are available to trace the source of recharge, groundwater residence times and flow pathways from surface waters and the unsaturated zone into the saturated zone. These include the use of geophysical techniques, chemical tracers and stable isotopes in water. An attractive and relatively new method for identifying sources of groundwater recharge from the human environment is the use of synthetic organic chemicals, here referred to as *micropollutants* (Jekel *et al*., 2015; Reh *et al*., 2015; Schirmer *et al*., 2011). The utility of this last method is being tested for a field-based case study in a small catchment in Switzerland.

2. Background and Methods

Micropollutants comprise a wide range of compounds including pharmaceutical chemicals, pesticides and personal care products. In this study, the use of micropollutants is explored as a basis to identify inputs of artificial recharge from sources including treated and untreated wastewater, stormwater-impacted streams and irrigation runoff. This is one facet of a larger objective of the study, which is to investigate changes in the water balance in a watershed with significant anthropogenic impact.

The use of micropollutants as anthropogenic tracers is appealing for several reasons. Firstly, these products are absent in the natural environment, so that their presence unequivocally indicates an anthropogenic input. Secondly, with recent increases in analytical power and detection technologies, it is possible to quantify many of these products on the order of nanograms per litre. Micropollutants are not conservative tracers, so their isolated interpretation for these purposes may be limited. However, they can be a powerful tool when used in combination with other physico-chemical tracers such as temperature measurements or stable isotopes (Moeck *et al*., 2017).

Often, databases for concentrations of groundwater micropollutants are censored – a proportion of detections may fall below a limit of detection or limit of quantitation. Choosing appropriate methods for working with censored datasets is a preliminary, yet often under-appreciated, step when working with these resources.

In order to estimate summary statistics and carry out further calculations for correlations or trend analysis, care must be taken to avoid introducing unnecessary bias (Helsel, 2012). Non-parametric methods are a suitable method to estimate summary statistics, accounting for knowledge about values on either side of a detection limit. A non-parametric, interval-censoring approach has been applied in this study.

3. Case Study

The concepts in this study are being tested within a monitoring network in a shallow, unconfined fluvio-glacial aquifer located in the upper half of the Kempt river catchment in the canton of Zürich, Switzerland. The Kempt is a tributary to the Töss, which is in turn a tributary to the Rhine. The upper Kempt catchment is approximately 10 km^2 in area and the aquifer is approximately 8 km^2 with variable thickness ranging from 10 to 20 m. Most of the groundwater body underlies the Swiss municipality of Fehraltorf, which consists of a small urban area (approximately 20% land cover) and a significant agricultural area (>50% land cover). The Kempt aquifer is actively exploited for municipal water supply and agriculture in Fehraltorf and several other surrounding municipalities.

This bulletin was prepared by Robin Weatherl from Eawag with assistance from Prof. Mario Schirmer, Eawag and University of Neuchâtel. For further information please email: Robin.Weatherl@eawag.ch

Inspiration

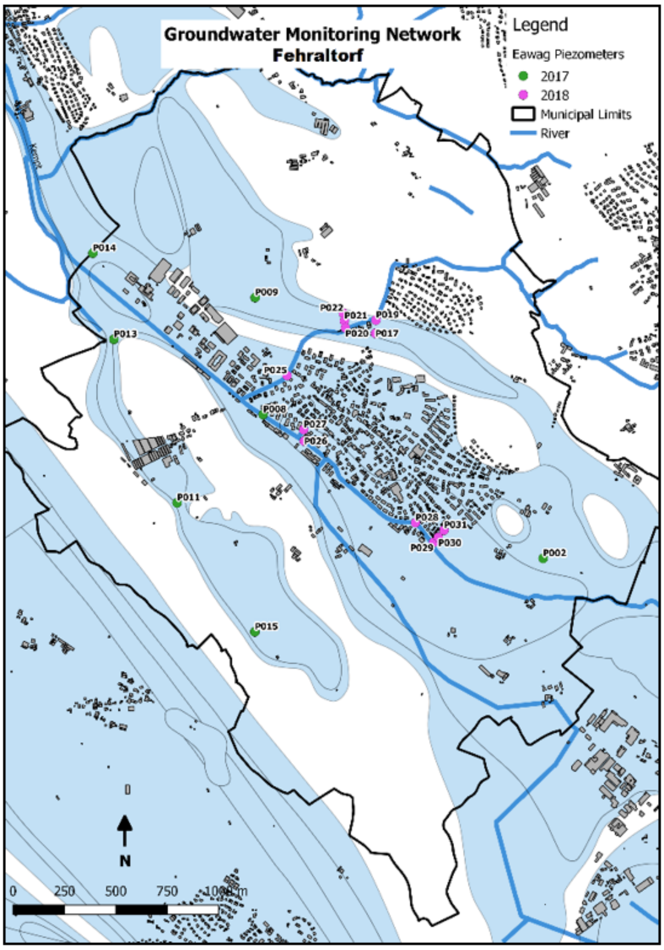

Figure 1: Shallow groundwater monitoring wells installed in Fehraltorf through the course of this study. The main body of the aquifer is shaded in light blue.

There exist 8 wells and 2 cantonal wells of depths between 5-20 m in Fehraltorf. For the purpose of this study, an additional network of 19 supplementary shallow wells (between 5-8 m depth) were installed between 2017 and 2018. The location of the wells within the watershed and municipality is shown in Figure 1.

Sampling campaigns for micropollutant analysis are being carried out on a seasonal basis, beginning in autumn 2017. Both groundwater and surface water samples are collected. Surface water analyses are extremely pertinent for proper interpretation of the groundwater due to variable groundwater-surface water interactions over the length of the river and seasonal variations.

Samples are analysed for 30 different products using targeted analyses liquid chromatography tandem mass spectrometry. The products measured include pesticides, pharmaceutical chemicals and industrial or mixed-use products.

4. Results and Discussion

Summary statistics for a selected number of frequently detected micropollutants at two different points in time are shown in Figures 2-4. These images summarise concentration percentiles, i.e. how many samples are in the top 75%, 50%, and 25% of all concentrations measured. Results from late spring and summer 2018 are provided to illustrate any temporal changes in concentrations. The products depicted below are thought to represent a variety of sources (for example precipitation or leakage from water pipes) and processes (for example infiltration, runoff, or groundwater-surface water interactions) within Fehraltorf. It should be noted that the sample size of these results is variable: between 7 and 15 samples are included in the groundwater estimates, whereas the sample size for surface waters varies between 5 and 7 data points.

Caffeine can be a useful indicator for untreated wastewater in groundwater (Panasiuk *et al.*, 2015). Notable examples of untreated wastewater into groundwater include leakage from septic tanks, or sewer networks, or from combined-sewer overflow. *Caffeine* has high removal rates from wastewater treatment plants and so is not usually present in treated effluent. The results shown in Figure 2 suggest an active source of *caffeine* into catchment waters during the spring months. It is hypothesised that this source is the combined sewer systems on site, which have a potential to overflow during heavy storms. High concentrations detected in groundwater in May suggest that overflow is able to rapidly infiltrate into the groundwater, within a matter of weeks. The concentrations detected in July are orders of magnitude lower than those measured in the spring months.

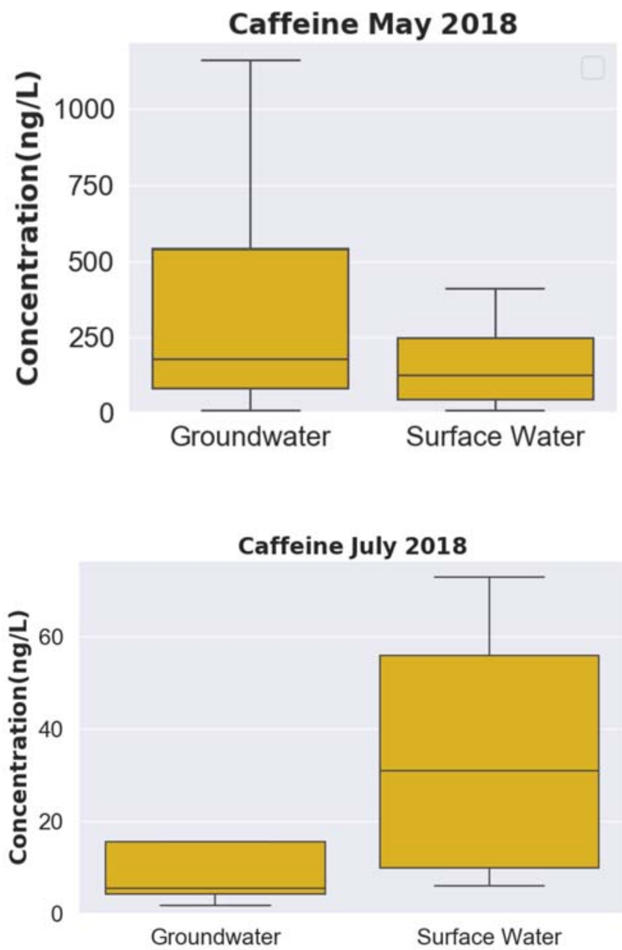

Figure 2: Concentrations of *caffeine* measured in groundwater and surface water in Fehraltorf. *Caffeine* is an indicator for untreated wastewater in the environment.

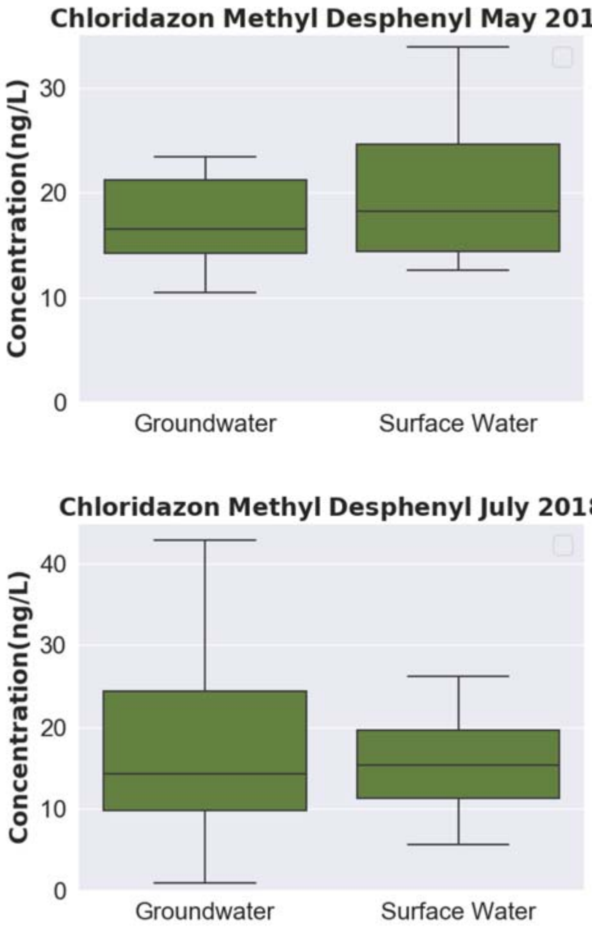

Figure 3: Concentrations of the herbicide degradation product *chloridazon methyl desphenyl* in Fehraltorf. This herbicide is thought to be an indicator for agricultural runoff.

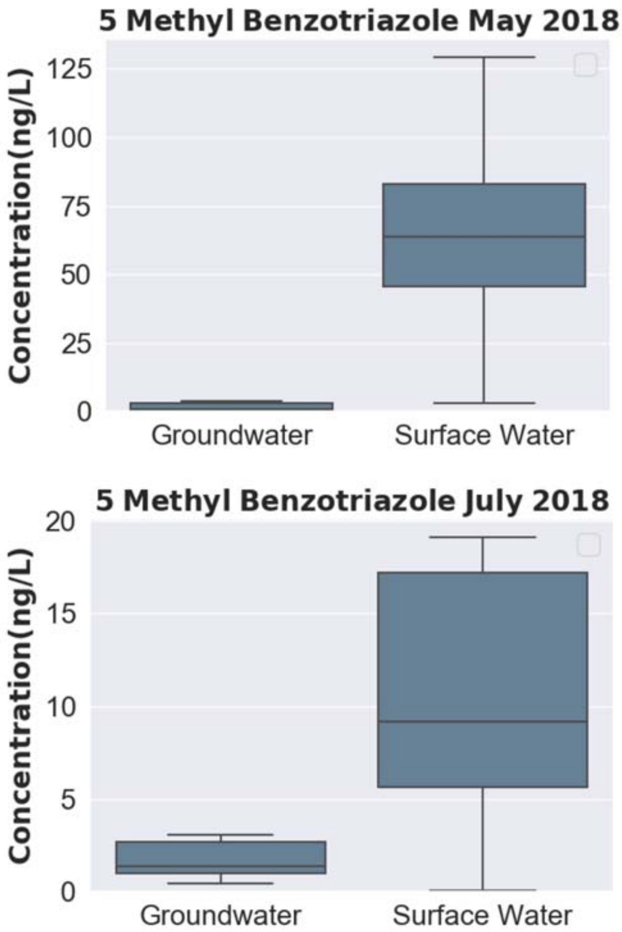

Figure 4: Concentrations of *5-methyl-benzotriazole* measured in Fehraltorf. *Benzotriazole* is mainly thought to be an indicator of industrial activity.

Figure 3 shows results of *chloridazon methyl desphenyl* (CMD) concentrations measured over time in groundwater and surface water. CMD is a degradation product of the herbicide *n-chloridazon*. The parent product is known to be mobile in many soil types and CMD is a known major transformation product. In most cases *n-chloridazon* is applied to fields early in the planting season and has a half-life of <8 weeks (Buttiglieri *et al*., 2009). It is thought that CMD originates from agricultural runoff during the months of April and May. The relatively constant median concentrations suggest a somewhat stable state of this degradation product once it reaches the groundwater.

A final example is given in Figure 4, showing concentration changes of *5-methyl-benzotriazole* (5MB) at the Fehraltorf field site. Among a variety of uses, it is known to be applied as a de-icing agent and a corrosion inhibitor. Groundwater concentrations are relatively low and stable. Surface water concentrations are both higher and more variable throughout the year, which supports the hypothesis that this product originates principally from outdoor applications. Interestingly, the highest concentrations of 5MB were found at surface water sites in close proximity to agricultural fields.

These comparisons of micropollutant concentrations in surface water versus groundwater during two seasons sheds some light on the source dynamics of such products. Results suggest that, despite differing pathways, the active sources of both urban and agricultural products occur during spring months. While it is not shown here, analyses from 2017 suggest the same hypothesis. It remains to be seen whether this trend will be upheld in 2019.

5. Conclusion

These results are only a first reconnaissance step in fully utilising the information gathered from micropollutants. In further publications, these data will be studied in greater depth to explore their utility as process indicators (via parent-to-degradates ratios). The results of these analyses will also be combined with stable isotope data from groundwater and surface water, in order to verify or refute some of the hypotheses on their sources.

Acknowledgments

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