



# Investigating the dynamics of two herbicides at a karst spring in Germany: Consequences for sustainable raw water management



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## HIGHLIGHTS

- Atrazine can almost always be detected in spring water.
- Metazachlor is only detectable after recharge events and not in winter.
- Atrazine, inorganic cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) and the electrical conductivity correlate.
- The long-term storage potential of karst aquifers may not be ignored.
- Persistent substances are prone to cause long-term contamination in karst systems.

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## ABSTRACT

While karst aquifers are considered as rapid flow and transport systems, their high potential for long-term storage is often ignored. However, to achieve a sustainable raw water quality for drinking water production, the understanding of this potential is highly essential. In this study, the transport dynamics of the two herbicides metazachlor and atrazine as well as a degradation product of the latter (desethylatrazine) were investigated at a karst spring over 1 year. Even 20 years after its ban in Germany, atrazine and its degradation product were almost always detectable in the spring water in the low  $\text{ng L}^{-1}$  range (up to  $5.2 \text{ ng L}^{-1}$ ). Metazachlor could only be detected after precipitation events, and the observed concentrations (up to  $82.9 \text{ ng L}^{-1}$ ) are significantly higher than atrazine or desethylatrazine. Comparing the dynamics of the herbicides with the inorganic ions  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and electrical conductivity, a positive correlation of atrazine with these parameters could be observed. From this observation, atrazine is concluded to be located within the aquifer matrix. To achieve a sustainable raw water management at karst springs, the rapidness of these systems needs to be highlighted as well as their long-term storage potential. Persistent substances or transformation products are prone to deteriorate the raw water quality for decades.

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## 1. Introduction

In the *Guidelines for Drinking-Water Quality*, the World Health Organisation emphasises the advantages and necessities of effective catchment management, i.e., understanding an aquifer and identifying possible water pollution scenarios affecting the raw water quality (WHO, 2011). The understanding of karst aquifers is particularly challenging due to their specific characteristics (e.g., dolines, conduit flow). Still, these highly dynamic and heterogeneous aquifer systems are important drinking water sources all over the world. The complex interaction between developed karst conduits including the related

rapid flow and transport processes in them (residence time of a few days, e.g., Pronk et al., 2009; Hillebrand et al., 2012a) and the high-volume porous rock matrix (characterised by slow matrix flow and long residence times of several years, e.g., Einsiedl, 2005) is not yet fully understood and thus still subject to research. Investigating the recharge mechanisms at a shallow karst system rapid preferential flow and diffuse matrix flow (which is characterised by much slower flow rates) were observed (Atkinson, 1977; Haria et al., 2003). However, for some deep aquifers, only slow matrix flow could be identified (Haria et al., 2003; Chilton et al., 2005).

It is a long established fact that recharge events in karst systems lead to strong variations in spring water quality (Jakucs, 1959). Monitoring these spring signals in terms of physical or chemical parameters allows for the integral characterisation of the total catchment area. This feature has been used to, e.g., determine the mean residence time of water within aquifer systems based on tritium data (Maloszewski et al.,

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2002) or to estimate the total amount of wastewater infiltrating such systems by employing caffeine as a semi-quantitative indicator (Hillebrand et al., 2012a). Stueber and Criss (2005) derived the primary immediate sources for water quality components depending on their covariance with the electrical conductivity (EC) or the turbidity. A positive covariance of components time series with the EC implies diffuse (matrix) flow being its primary source, while a positive covariance with turbidity suggests that the components immediate source was from agricultural fields.

In the presented work, two herbicides (atrazine and metazachlor) and the degradation product desethylatrazine are employed, in order to improve the understanding of spring water signals after precipitation events and consequently the understanding of the investigated karst aquifer system, which are vital for providing measures for sustainable raw water quality. Atrazine is one of the most widely used soil and weed herbicides, whereas its use has been prohibited in Germany since 1992. However, it is well dispersed and can still be found in the environment even after more than 20 years (Jablonowski et al., 2011; Nödler et al., 2013; Reh et al., 2013). The potential of atrazine to be degraded in karst aquifers is stated to be very little to non-existent (Johnson et al., 2000; Chilton et al., 2005). One of its degradation products is desethylatrazine (Kolpin et al., 1998). However, desethylatrazine is also formed from other triazine herbicides like propazine (Behki and Khan, 1994). Atrazine is affected by sorption, exhibiting a low desorption rate, which may take several days or even weeks (Dehghani et al., 2005). In contrast to the banned substance atrazine, the weed control agent metazachlor is approved in Germany. Its tendency to adsorb onto soil material is known to be low (Mamy and Barriuso, 2005), while being readily degradable (Allen and Walker, 1987; Beulke and Malkomes, 2001). In the investigated karst system, transport is known to be rapid and an appearance of metazachlor in spring water can still be expected. For reference purposes and to locate the origin of atrazine, desethylatrazine and metazachlor, the time series of these three compounds are compared to the time series of the inorganic ions nitrate ( $\text{NO}_3^-$ ), calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ) as well as the EC of the spring water.

The aims of the study are (i) to improve the understanding of contaminant migration in karst aquifers under consideration of recent and former herbicide applications, (ii) to highlight the long-term storage potential of karst aquifers and (iii) to draw attention to the consequences of unsustainable herbicide application for the raw water quality. The authors hypothesise that the characteristic residence time distribution of water in karst aquifer systems (days to several decades) is reflected in the occurrence and dynamics of the investigated herbicides.

## 2. Materials and methods

### 2.1. Field work

#### 2.1.1. Study area

The investigated karst spring is the Gallusquelle, which is located in Southwest Germany (Fig. 1). It is used as a drinking water source for 40,000 people. Its average discharge is  $500 \text{ L s}^{-1}$ , draining a rural catchment (4,000 inhabitants) of approximately  $45 \text{ km}^2$ . Around 40% of the catchment is used for agriculture. These areas are used as grasslands and for the cultivation of crops (approximately 14% of the total catchment area; Sauter, 1992). Despite the thick unsaturated zone ( $\sim 100 \text{ m}$ , Fig. 1) within the investigated system, precipitation can quickly reach the groundwater through dolines and dry valleys as concentrated recharge. Through these preferential flow paths, the transport of solutes including contaminants from the ground surface toward the spring is enhanced. The occurrence of contaminants only days after precipitation events has been shown in former investigations (Heinz et al., 2009; Hillebrand et al., 2012b). In contrast, a mean groundwater residence time of more than 20 years was determined by Geyer et al.

(2011) employing lumped parameter modelling of tritium in spring water.

#### 2.1.2. Sampling

Over the period of nearly 1 year, a total of 263 spring water samples were collected and analysed for herbicides from March 6, 2010, until February 16, 2011. The sampling rate varied between weekly, daily and multiple daily depending on the spring discharge and the occurrence of recharge events. For one recharge event, a highly increased sampling rate of up to 8 samples per day was realised. Selected major ions concentrations were determined over a period of 3 months, including the mentioned recharge event ( $n = 153$ ). Additionally, a rain water sample was collected during that recharge event with a precipitation-totalisator (accumulative precipitation gauge) for the hydrograph separation. To ensure the stability of the analytes, the samples were stored at  $4 \text{ }^\circ\text{C}$ . For herbicides, samples were preconcentrated by solid phase extraction (SPE) within 48 h and the SPE cartridges were stored at  $-18 \text{ }^\circ\text{C}$  until analysis (Hillebrand et al., 2013).

### 2.2. Chemicals

Methanol (LC/MS grade) was purchased from Fisher Scientific (Schwerte, Germany), and ammonium acetate, ethyl acetate, formic acid, potassium dihydrogen phosphate and disodium hydrogen phosphate dihydrate (all analytical grade) were purchased from VWR (Darmstadt, Germany). Atrazine, atrazine- $\text{D}_5$ , desethylatrazine and metazachlor were purchased from Dr. Ehrenstorfer (Augsburg, Germany), and carbamazepine- $\text{D}_{10}$  was purchased from Promochem (Wesel, Germany).

### 2.3. Laboratory and on-site analyses

#### 2.3.1. On-site analysis

Hourly data for electrical conductivity (reference temperature:  $20 \text{ }^\circ\text{C}$ ) and turbidity of the spring water as well as the spring water levels were gauged with an installed continuous monitoring system. The water levels were transferred into spring discharge data, applying a rating curve.

#### 2.3.2. Inorganic ions

The samples for cation analysis were acidified with methane sulfonic acid ( $2.5 \mu\text{L mL}^{-1}$ ). The analysis for the inorganic ions was performed by ion chromatography (IC) as described in Nödler et al. (2011).

#### 2.3.3. Herbicides

The analytical method for the determination of the herbicides metazachlor and atrazine as well as its degradation product desethylatrazine is based on SPE and high-performance liquid chromatographic separation coupled with tandem mass spectrometric detection (HPLC/MS-MS). The details of the method have been published earlier (Nödler et al., 2010). Briefly, a sample volume of 500 mL was buffered at neutral pH (phosphate buffer), spiked with 100 ng atrazine- $\text{D}_5$  and carbamazepine- $\text{D}_{10}$  and extracted by SPE (500 mg Oasis HLB, Waters, Eschborn, Germany). After extraction, the cartridges were rinsed with ultrapure water, dried, wrapped in aluminium foil and kept frozen ( $-18 \text{ }^\circ\text{C}$ ) until analysis. Prior to analysis, the herbicides were successively eluted from the sorbent with methanol and ethyl acetate. The eluate was evaporated and re-dissolved in a 5 mM ammonium acetate aqueous solution, containing 4% methanol. Unlike Nödler et al. (2010), only 0.8 mL was used to re-dissolve the analytes. Thus, a higher enrichment factor and consequently lower method detection and quantification limits were achieved: the method detection limits (MDL) of atrazine, desethylatrazine and metazachlor were 0.3, 0.4 and  $0.5 \text{ ng L}^{-1}$ , respectively. The method quantification limits (MQL) were  $1.1 \text{ ng L}^{-1}$  for atrazine and  $1.4 \text{ ng L}^{-1}$  for desethylatrazine and

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