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# Riverbank filtration of micropollutants

A wide variety of micropollutants from Swiss rivers can be found in bank filtrate. While many micropollutants are degraded or retarded as they pass through the subsurface, certain persistent substances end up in drinking water. Even though they do not occur in concentrations hazardous to human health, inputs of these substances to surface waters should be minimized.

For some decades, Swiss water suppliers have been using bank filtrate – with minimal treatment – to produce drinking water. At the same time, we know that chemicals used in households, agriculture and industry are present at low concentrations in our rivers. The question thus arises whether bank filtration systems serve as an adequate filter for such contaminants. It needs to be borne in mind that conditions in rivers and banks can vary widely. Under high-discharge conditions, for example, concentrations of substances in the river are quite different (see also p. 8), as is the passage of water through the infiltration zone. The concentration dynamics in the river is reflected in the groundwater in an attenuated form, given the travel time from river to groundwater (ranging from several days to weeks).

## Biodegradation difficult to predict

The behaviour of substances during their passage through the infiltration zone is not only determined by the environmental conditions: depending on their particular properties, substances may be biologically – or, more rarely, chemically – degraded, they may be adsorbed and retarded by aquifer material, or they may reach the well merely diluted by groundwater (Fig. 1). It remains difficult to predict the biological degradation of pollutants by microorganisms in soil or water on the basis of their molecular structure. The transformation products may not necessarily be less relevant than the original compounds. In general, more substances can be degraded in the presence of oxygen. According to the literature, however, certain substances, such as the antibiotic sulfamethoxazole, are more readily degraded under anoxic conditions. In Switzerland, the predominantly sandy-gravel infiltration zones and aquifers, together with the low content of dissolved organic matter in river water, generally promote oxic conditions. In the future, however, climate change – with higher temperatures and less precipitation – may increasingly give rise to anoxic conditions, as indeed occurred during the summer heatwave of 2003 (see p. 16). This could also impair the degradation of organic compounds.

In the degradation of pollutants, purely chemical reactions are of less relevance; if they do occur, they generally take the form of hydrolysis. This (pH-dependent) reaction can be readily predicted and is tabulat-

ed for many substances. Sorption of organic compounds will mainly be to organic matter and will be more intense, the more hydrophobic the compound is. Serving as a measure of hydrophobicity is the octanol-water distribution coefficient ( $K_{ow}$ ). Neutral compounds with a ( $K_{ow}$ ) greater than 1000 will be retarded to a certain extent. Cationic compounds may also interact with (sometimes negatively charged) organic matter, while polar anionic compounds are not retarded at all.

In general, dilution with groundwater plays an increasingly important role, the further the well is from the river. However, in many alluvial zones – e.g. the Thur floodplain – the groundwater tends to be former river water which has simply infiltrated elsewhere. Using indicators such as conductivity or temperature, hydrologists can determine the flow paths from river to groundwater and the age of the water (see p. 4).

## Around 100 organic micropollutants in bank filtrate

As part of the “Restored corridor dynamics” (RECORD) project, we investigated the fate of pharmaceuticals and pesticides during their

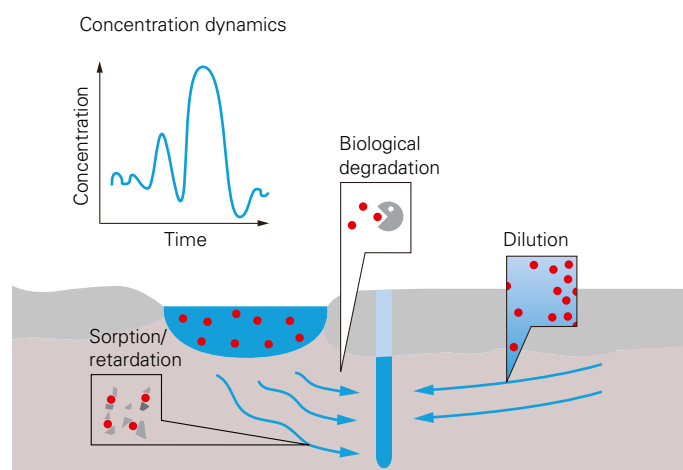


Fig. 1: Schematic representation of bank filtration from river to groundwater well, showing key processes that can lead to changes in pollutant concentrations.

passage from river to groundwater in the Thur floodplain. This sub-project was funded by the Federal Office for the Environment. As a prealpine river, the Thur exhibits considerable fluctuations in water levels. In addition, the travel time from river to groundwater well only amounts to a few days. Accordingly, in contrast to earlier studies, samples were collected at a high temporal resolution under various conditions. In order to identify the relevant substances and to determine the effectiveness of filtration during subsurface passage at a field site in Niederneunforn (Canton Thurgau), a total of 3 river water samples and 32 samples of groundwater from adjacent transects were collected at various times of the year (Fig. 2). One-litre samples were first enriched using solid-phase extraction; separation was then performed by means of liquid chromatography, and individual compounds were detected using high-resolution mass spectrometry. With this method, it was possible for 250 different compounds to be simultaneously determined; today, as many as 500 can be detected [1]. The focus of our study was on pesticides, pharmaceuticals, biocides, corrosion inhibitors, artificial sweeteners and a number of transformation products. Almost 100 substances were found at concentrations ranging from 0.1 to 400 nanograms per litre. While similar numbers of substances were detected in river and groundwater, the concentrations in groundwater were generally lower (Fig. 3).

Around 60 per cent of the substances detected in river water – and even 72 per cent in groundwater – occurred in concentrations of less than 10 nanograms per litre. If the concentrations are summed, the average value was  $1.3 (\pm 0.5)$  micrograms per litre for river water and  $0.6 (\pm 0.2)$  micrograms per litre for groundwater. In groundwater, only three substances exceeded 100 nanograms per litre – the corrosion inhibitor benzotriazole, the artificial sweetener sucralose and the pesticide transformation product desphenylchloridazone.

#### Various pharmaceuticals eliminated in the infiltration zone

To investigate in more detail the passage of selected substances from river to groundwater during dry weather conditions, we collected samples from various wells along the direction of flow. A number of pharmaceuticals (diclofenac, atenolol, metoprolol, lidocaine) were found in river but not in groundwater, suggesting that these substances were eliminated. The concentrations observed in the wells nearest the river, with a very low water age of up to a day, were already considerably lower than in the river itself. The bulk of degradation would thus appear to occur in the initial infiltration zone. In contrast, the antiepileptic agent carbamazepine (known to be persistent), two of its metabolites and three other drugs – sulfamethoxazole, tramadol and venlafaxine – showed stable concentrations. These compounds were not degraded during subsurface passage



Fig. 2: The field site on the Thur, with detailed views of the groundwater transects in a restored and a channelized section (mean water age shown for selected wells).

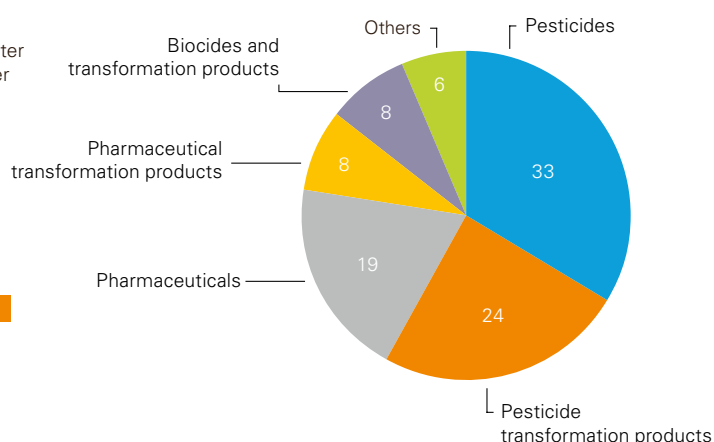
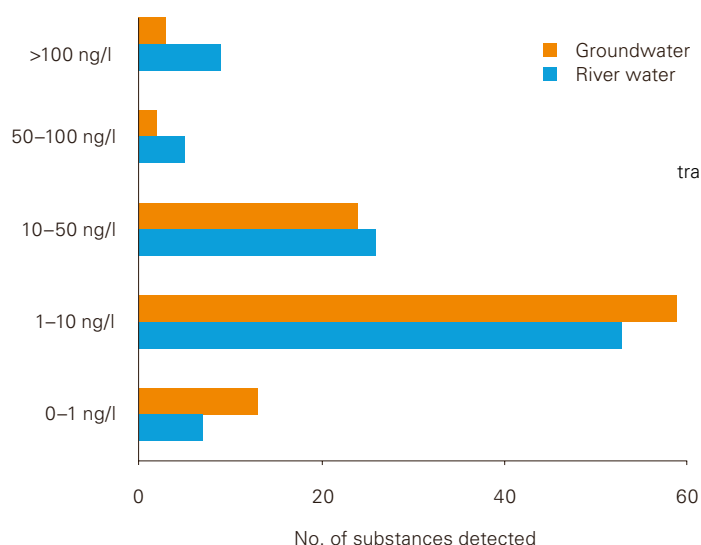


Fig. 3: Number of substances detected (98 of 250 investigated) in Thur river water and nearby groundwater by concentration range (left) and by category (right).

and were also detected in the groundwater well. These findings are in agreement with investigations of other bank filtrates carried out by the Canton Zurich Office for Waste, Water, Energy and Air (AWEL) [2], with our own ongoing analyses in Canton Basel-Landschaft and with studies performed in Germany [3]. According to the current state of knowledge, these low concentrations do not pose a risk to human health. However, under the Waters Protection Ordinance, persistent substances are considered to be generally undesirable. They can be largely eliminated by oxidation or activated carbon treatment (p. 30).

#### Behaviour under high-discharge conditions

To study the fate of compounds under high-discharge conditions, we analysed river water regularly collected by automated samplers during a series of flood events within the pesticide application season in the spring of 2010. Over a twelve-day period, groundwater samples were manually collected from observation wells along the two transects in the channelized and restored river sections (Fig. 4). The concentration dynamics for various substances under high-discharge conditions are shown in Fig. 5. Considerable quantities of the herbicide methyl chlorophenoxy acetic acid (MCPA) entered the Thur, presumably washed off the newly sprayed fields by rainwater. Even so, MCPA only occurred at concentrations above the limit of detection (1 nanogram per litre) in groundwater with a water age of less than a day. Freshly infiltrated river water is scarcely diluted, and this highly polar compound (anionic,  $\log K_{ow} = 2.4$ ) does not undergo sorption; thus, MCPA is biologically degraded in the infiltration zone with a half-life of just a few hours. In contrast, the pharmaceutical substances carbamazepine and 4-acetamidoantipyrine in the river were more highly diluted than usual because of the high-discharge conditions. For this reason, it is important to consider the residence time in the infiltration zone when interpreting the groundwater concentrations. The persistent compound carbamazepine – as under low-discharge conditions – showed no decrease in concentrations in groundwater. The polar compound 4-acetamidoantipyrine ( $\log K_{ow} = 0.15$ ), however, being degraded,

declined to below 20 per cent of the river water concentrations. This is in accordance with studies performed on another section of the Thur and with other studies [4].

#### Detailed analysis of degradation thanks to push-pull tests

In order to gain a better understanding of micropollutant elimination and to determine in situ microbial degradation rates, we conducted so-called push-pull tests (with the permission of the cantonal authorities) in a number of wells at some distance from the drinking water well [5]. For each test, fluorescein dye was added to 500 litres of groundwater, together with a number of readily degradable compounds (MCPA, 2,4-dichlorophenoxyacetic acid, mecoprop, atenolol, metoprolol and diclofenac), with a final concentration of 100 nanograms per litre for each substance. This solution was pumped into an observation well and, after 0.5–4 hours, pumped out again. The dye remaining in the pumped groundwater indicates to what extent the solution has been diluted in the aquifer. Because none of the compounds (given their properties) undergo sorption in the subsurface, any additional percentage decrease in their concentrations can be attributed to biological degradation.

Using a simple flow model, we were able to determine the half-lives for in situ degradation. Ranging from 0.5 to 6.7 hours, they demonstrate that the self-cleansing potential of the infiltration zone is remarkably high for these degradable substances. Supporting this is the almost complete formation of the transformation product atenolol acid from metoprolol and atenolol; at the same time, however, this shows that transformation products – depending on their ecotoxicological properties – may also be problematic. In a test performed during the winter, when the groundwater temperature was only 4°C, no appreciable degradation occurred; presumably, this was because microbial processes were slowed down by the low temperature. This finding confirms that degradation is significantly influenced by boundary conditions such as temperature.



### Minimizing pollution – despite safe drinking water

The studies described above show that a wide variety of micropollutants which can be found in Swiss rivers enter bank filtrate. Under appropriate conditions, however – i.e. if the temperature is high enough and sufficient oxygen is available – many of these substances are degraded by microorganisms, as was demonstrated on the Thur. We are currently analysing findings obtained at further sites in Canton Basel-Landschaft. In spite of degradation and sorption, certain persistent substances end up in drinking water. It is therefore imperative that concentrations of pollutants in surface waters should be kept as low as possible. Particularly effective are measures to minimize inputs from agriculture and to improve the removal of micropollutants at wastewater treatment plants. These measures also have positive effects on aquatic organisms. They could become increasingly important in the future, as climate change may possibly lead to lower dilution of contaminants in rivers. The requirement of a minimum travel time of ten days for infiltrating river water also has to be complied with in restored areas. This ensures that pathogens are sufficiently removed and micropollutants adequately degraded. In addition, it gives water suppliers time to respond to extreme events. As well as an improved self-cleansing capacity, restored river corridors offer enhanced recreational value and increased biodiversity. The low concentrations (nanograms-per-litre range) at which certain substances occur in drinking water would appear not to be hazardous to human health. They are well below the concentrations of contaminants typically found in food. As a general principle, however, persistent synthetic compounds are undesirable in natural waters and in drinking water. With appropriate treatment methods, levels of contaminants can be further reduced.

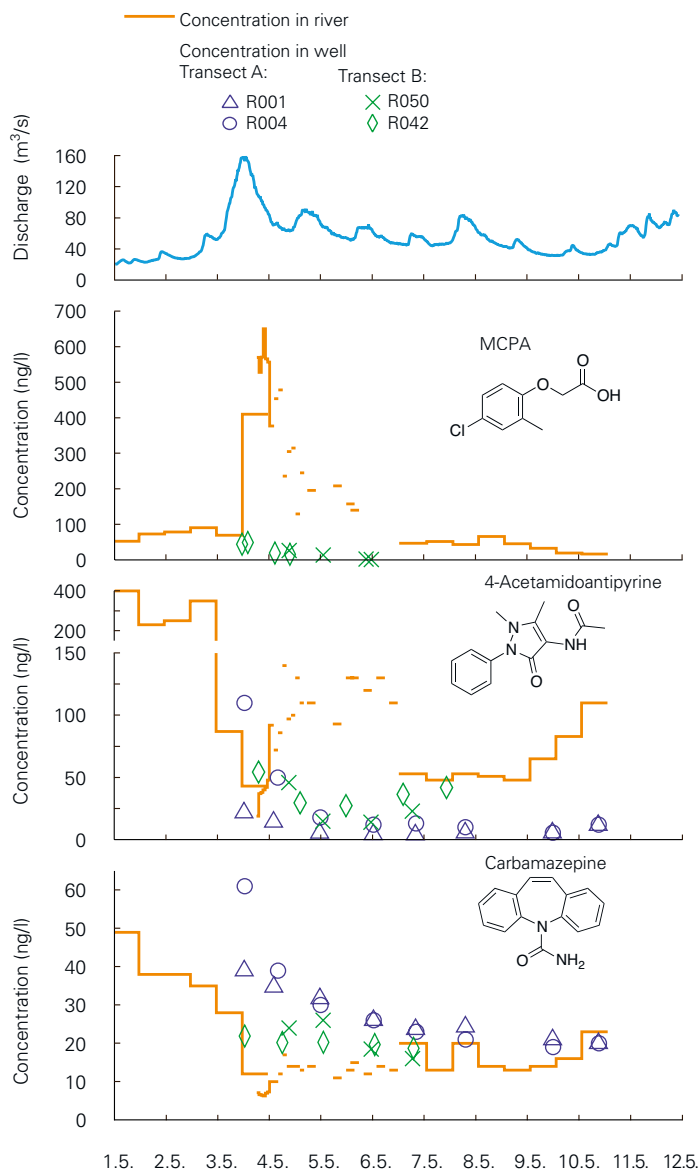


Fig. 5: Concentration/time curves for various substances in river and groundwater under high-discharge conditions during 2010; the substances selected are highly (MCPA), readily (4-acetamidoantipyrine) and poorly degradable (carbamazepine).



Fig. 4: Equipment used for manual collection of groundwater samples at various depths in an observation well. ((photo: Sebastian Huntscha))

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