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Accumulation of pharmaceuticals in groundwater under arid climate conditions – Results from unsaturated column experiments

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HIGHLIGHTS

- Evaporative enrichment of pharmaceuticals was demonstrated in unsaturated columns.
- Outflowing concentrations were higher than the inflowing for inhibited microbiology.
- Pharmaceutical enrichment occurred at the same rate like chloride.
- Microbiological degradation of carbamazepine was higher at 35 °C compared to 20 °C.
- Uninhibited columns showed the potential to remove the easy degradable bezafibrate.

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ABSTRACT

Intense reuse of treated wastewater in agriculture is practiced all over the world, especially in arid and water-scarce regions. In doing so, pharmaceutical residues in the water are irrigated to the soil and subsequently can percolate into the local aquifers. Since evaporation rates in these areas are typically high, persistent substances might enrich in the groundwater recharge of closed catchments like the Jordan Valley. Against this background, unsaturated column tests were conducted to investigate the potential for evaporative accumulation of the two pharmaceuticals bezafibrate and carbamazepine under simulated arid climate conditions. Parallel tests were conducted with inhibited microbiological activity where both substances showed an increase in the effluent concentrations proportional to the evaporation loss of the inflow solution. The mean accumulation factors of the pharmaceuticals correspond to the evaporated water loss. The experiments indicate the accumulation potential for pharmaceuticals with high persistence against biodegradation. For the first time, the overall potential for evaporative enrichment could be demonstrated for pharmaceuticals. Under the given experimental conditions, the two investigated pharmaceuticals did not enrich faster than chloride, which might result in soil salting prior to reaching harmful pharmaceutical concentrations in soil water. The findings are relevant to future assessments of environmental impacts of persistent trace substances, which need to take into account that concentrations in the aquatic cycle might increase further due to evaporative enrichment.

1. Introduction

The intensive use of treated wastewater in agriculture bears the potential of introducing emerging pollutants into the groundwater. Although some substances are degraded while percolating through the unsaturated zone, many persistent pharmaceuticals were found in aquifers underlying agricultural areas irrigated with treated wastewater (Kinney et al., 2006; Siemens et al., 2008; Avisar et al., 2009; Grossberger et al., 2014). Laboratory results indicate the potential of pharmaceuticals of reaching the groundwater after irrigation with treated wastewater as well (Chefetz et al., 2008; Siemens et al., 2010). Recent monitoring results in the Lower Jordan Valley (LJV) showed higher pharmaceutical concentrations in groundwater than in the infiltrating surface water (Wolf et al.,

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2009). As irrigation is mostly applied in dry climates, such substances could be assumed to accumulate in the shallow groundwater due to high evaporation rates in semi-arid areas. For the LJV, the short-cycled agricultural use of mixtures of treated wastewater with the locally pumped groundwater, combined with the closed character of the catchment with the Dead Sea as final sink, supports an enrichment as well. Nevertheless, the issue of evaporative accumulation of pharmaceutical substances has not been addressed to date.

Pharmaceuticals in the aquatic environment are ubiquitous and their negative effects at environmental concentrations were already reported for e.g. fish (Kidd et al., 2007; Pomati et al., 2008; Brodin et al., 2013). However, after treatment, levels of residues in drinking water are very low and are considered unproblematic (Webb et al., 2003; Schwab et al., 2005; Houeto et al., 2012). Due to the assumed accumulation, environmental concentrations might increase to up to harmful levels and therefore entail increasing effort for drinking water treatment.

Against this background, the hypothesis of accumulating pharmaceutical concentrations over time was investigated following two approaches: Long-term field investigations and small-scale column studies at lab scale. While the field studies were insufficient to provide statistically valid evidence for the Lower Jordan Valley (Zemann et al., 2014), the studies showed that the tempo-spatial distributions of x-ray contrast media concentrations were most likely due to shifting medication and application patterns in this area (Zemann et al., 2015). However, the idea of accumulating persistent substances by evaporation processes, e.g. similar to salt enrichment during salting of soil, seems still realistic. The increase in pharmaceutical concentrations in wastewater-irrigated soils was already investigated in China (Chen et al., 2011) and Tunisia (Fenet et al., 2012). Soils irrigated with treated wastewater in Colorado (USA) showed rising carbamazepine (CBZ) concentrations after several months of irrigation, while the soil organic matter (SOM) was assumed to be the controlling factor for pharmaceutical retention (Kinney et al., 2006). However, none of these studies considered evaporative processes.

The experiments of this study were conducted under most realistic natural conditions, i.e. by choosing temperatures, humidity and irrigation rates as they were measured in the LJV (Ministry of Water and Irrigation (2004)). In addition, this includes the use of real treated wastewater, the use of natural sand, and the consideration of the relevant processes, i.e. degradation and sorption under unsaturated flow conditions. Substances were selected according to the range of pharmaceuticals detected in previous studies in the LJV (Zemann et al., 2014). Out of this spectrum, pharmaceuticals with different persistence against biodegradation were selected. Those were the rather easily biodegradable lipid lowering agent bezafibrate (BEZ) and the antiepileptic CBZ. Their degradability (BEZ) and persistence (CBZ) was reported by different authors, e.g. (Maeng et al., 2011; Grossberger et al., 2014; Rühmland et al., 2015).

2. Methodology

2.1. Experimental setup and conceptual idea

The experiments were conducted in six stainless steel columns filled with prewashed quartzous sand and packed by a pounder. Relevant experimental characteristics are listed in Table 1. Each column had a percolation length of 50 cm and a diameter of 10 cm, with a total volume of 3695 cm^3. A ceramic filter plate at the outlet prevented leaching of sand and a potential clogging of the outflow pipe and led to uniform drainage at the column bottom. The grain size of the used sand was determined as medium-fine sand with shares of fine sand (57%), medium sand (41%), coarse sand (~1%), and silt (~1%), respectively. The hydraulic conductivity of $3*10^{-4}$ m/s was determined according to Hazen from the grain size distribution. Each column was spiked with four equally distributed soil moisture sensors (ECH2O EC-5) from UMS Co. as shown in the supplementary materials (SM 1, left).

Table 1
Physio-chemical soil parameters and experimental conditions for all columns.

Soil properties			Column conditions		
p_s	[g/cm]	2.65	L	[cm]	50
n	[%]	36	A	[cm^2]	73.9
k_f	[m/s]	$3*10^{-4}$	Q	[ml/day]	108
C_{org}	[wt.%]	0.13–0.23	T	[°C]	30
			Φ	[%]	45
			C_0	[µg/l]	20

p_s = Grain density.
n = Porosity.
k_f = Hydraulic conductivity.
C_{org} = Carbon content.
L = Length.
A = Surface area.
Q = Flow rate.
T = Temperature.
Φ = Humidity.
C_0 = Spiked pharmaceutical concentration.

All columns were operated under unsaturated conditions. The feeding solution was trickled onto the top of each column by four cannulas at a distance of 1 cm (see SM1, left). The feeding solution was stored in a fridge and supplied to the columns by a peristaltic pump via stainless-steel pipes 0.5 mm in diameter (SM1, bottom right). The specified pumping rate according to the hose diameter (0.51 mm) was 108 ml/day. This rate features a mean daily irrigation amount used by farmers in the LJV (Ministry of Water and Irrigation (2004)). The effluent of each column was pumped back to the fridge where it was stored as a collective sample in separated glass bottles. The columns were placed on a table in one row (SM1, top right). Of the six columns, respectively three were operated under the same conditions to obtain replicate results. Column numbers I1, I2 and I3 (I = inhibited) were operated with a toxic feeding solution to inhibit microbiological activities during percolation. The columns operated under normal, uninhibited conditions were labeled U1, U2 and U3 (U = uninhibited). Columns U3 and I3 did not have internal monitoring facilities. The three inhibited and the three uninhibited columns were each fed from the same storage bottle. Subsequently, the inflowing amount of each column was calculated from mean weight differences of the feeding solution bottles divided by three and related to the share of the effluent at each column.

To obtain semi-arid evaporation conditions, the whole experiment was built inside a climatic chamber (approx. 2.5 m × 4 m) adjustable for temperature and humidity. The temperature was kept at 30 °C and the humidity at 45% during the whole experiment. The numbers were chosen according to mean values for the LJV (Ministry of Water and Irrigation (2004)). Beside the sampling and control times, the room was kept dark to avoid any photochemical degradation processes. During the whole experiment, the columns were placed on scales to monitor the water balance.

The feeding solutions consisted of treated wastewater from a local wastewater treatment plant (WWTP) in Karlsruhe Neureut and were spiked with the investigated pharmaceuticals and LiBr as conservative tracer. Pharmaceuticals were added to a concentration of 20 µg/l from an aqueous stock solution. Residual concentrations in the treated wastewater might even increase this concentration. The feed solution of three columns was acidified with NaN_3 (0.1%) to inhibit microbiological degradation and growth. This feeding