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Biodegradation of Pharmaceutical Compounds and their Occurrence in the Jordan Valley

Andreas Tiehm · Natalie Schmidt · Michael Stieber · Frank Sacher · Leif Wolf · Heinz Hoetzl

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Abstract In particular in arid regions the reuse of waste water and aquifer recharge is an important issue. Elimination of persistent emerging pollutants represents a key factor in integrated water resources management, and identifying suitable treatment processes to eliminate such compounds becomes inevitably necessary. It is the objective of this study (1) to assess the occurrence of emerging pollutants in the Jordan Valley and (2) to review and examine the biodegradability of selected key compounds. Among the most frequently detected compounds during a sampling campaign in 2007 were pharmaceutical residues such as carbamazepine, diclofenac, or naproxen, and X-ray contrast agents such as diatrizoic acid and iopromide, all typically found in Europe and the USA as well. To gain further insight into elimination processes, biodegradation studies were conducted with batch tests and flow-through soil columns under unsaturated, aerobic conditions. Results demonstrated biodegradation for pharmaceutical residues such as ibuprofen, diclofenac and bezafibrate. The degradation rate was faster in treated waste water as compared to raw waste water, most probably due to competing substrate consumption in raw waste water. The antiepileptic carbamazepine showed no degradation in the batch tests and only moderate removal during soil passage, probably due to sorption. The results of this study and previously published data emphasize the need for further studies under more defined conditions to elucidate the specific conditions under which biodegradation of emerging pollutants proceeds.

Keywords Aquifer recharge · Biodegradation · Carbamazepine · Diclofenac · Jordan Valley · Pharmaceutical residues · Waste water reuse

A. Tiehm (✉) · N. Schmidt · M. Stieber · F. Sacher
Water Technology Center (TZW), Karlsruher Str. 84, 76139 Karlsruhe, Germany
e-mail: andreas.tiehm@tzw.de

L. Wolf · H. Hoetzl
Department of Applied Geology (AGK), Karlsruhe Institute of Technology (KIT),
Kaiserstraße 12, 76128 Karlsruhe, Germany

1 Introduction

The release of emerging pollutants such as pharmaceutical compounds and their metabolites into the aquatic environment has become an issue of increasing concern over recent years. With urine being the major path of entry (Winker et al. 2008) more than 80 pharmaceuticals and some of their metabolites have been detected in influents and effluents of European and US waste water treatment plants (WWTPs). In minor concentrations some of these compounds also have been found in surface water and groundwater. Concentrations in the range of ng/L up to μg/L were reported in surface waters, e.g. diclofenac 0.01–5.5 μg/L, ibuprofen 0.005–7.1 μg/L, gemfibrozil 0.06–4.8 μg/L, carbamazepine 0.01–6.3 μg/L, or naproxen 0.01–5.2 μg/L (e.g. Sacher et al. 2001; Debska et al. 2004). In areas of extreme water scarcity next to the reassessment of the production of water intensive agricultural products (Mourad et al. 2009), waste water reuse in irrigation and artifical recharge of groundwater (Al-Sheriadeh et al. 1999; Eusuff and Lansey 2004; Al-Khashman 2009) are important measures to meet the increasing water demand in semi-arid regions. Waste water reuse can lead to the accumulation of persistent organic pollutants (POPs), e.g. pharmaceuticals, endocrine disruptors (e.g. Bisphenol A) or trialkylphosphates (e.g. tris(2-chloroethyl) phosphate), used as placticizers (Wintgens et al. 2008; Reemtsma et al. 2008; Zoller 2008). In this study, a sampling campaign was conducted to gain information on the occurrence and distribution of emerging pollutants in water samples of the Jordan Valley. In 2007 and 2008 waste water, surface water, and groundwater samples have been taken along the Jordan Valley. Selected results of the analytical screening program are presented in this paper. Biodegradation of specific compounds was studied on laboratory scale in batch experiments. Elimination of pharmaceutical residues and X-ray contrast agents additionally was examined in flow-through soil columns under unsaturated, aerobic conditions.

2 Materials and Methods

To elucidate the occurrence of emerging pollutants in Jordanian water sources, sampling campaigns have been carried out for anthropogenic trace organics most frequently detected in Europe or the USA. Afterwards biodegradation of selected compounds was tested in batch and soil column experiments in the laboratory to investigate possible elimination pathways during aquifer recharge and storage.

2.1 Sampling Campaign and Analysis

Within the period spring 2007 to spring 2008, grab samples of wastewater, surface water and groundwater have been collected from different sites at the Lower Jordan River Valley. Since WWTPs discharge into surface water, which infiltrates the groundwater, persistent organic pollutants were analyzed in the different water sources. After sampling the pH was adjusted to approx. 2 by adding hydrochloric acid to stabilize the samples for the transport to Germany. After dilution of the samples and solid phase extraction (SPE) with subsequent filtering in case of turbid extracts, the pharmaceutical residues including X-ray contrast agents were analyzed by two-fold injection in a HPLC-ESI-MS-MS system 1090, Series II from Agilent Technologies (Waldbronn, Germany), using a Luna C18 column (250 × 2 mm, 5 μm particle size) from Phenomenex (Aschaffenburg, Germany) for separation (Sacher et al. 2001, 2008).

2.2 Batch Experiments into Biodegradation of Emerging Pollutants

Using filtered raw waste water and treated waste water, two active batch tests and one control were set up to examine biodegradation in the presence of two different background concentrations of organic load. A mixture of emerging pollutants was added, containing 2–5 μg/L of each substance (pharmaceuticals, endocrine disrupters and trialkylphosphates). The active batches were inoculated with activated sludge from the WWTP Eggenstein–Leopoldshafen and incubated at room temperature under aerobic conditions through constant aeration. The control batches were set up in the same way, but autoclaved and cooled at <4°C. Microbiological analysis of bacteria by the most-probable-number (MPN) technique at the end of the experiment confirmed that no viable organisms were present in the control batches. The results for the elimination of pharmaceuticals shown in this study represent the calculated mean value of the two active assays in relation to the control.

2.3 Elimination of Emerging Pollutants during Soil Passage

Unsaturated column experiments were conducted to study biodegradation under vadose zone conditions (Fig. 1). Four columns of stainless steel, filled with natural vadose zone sediment, were irrigated with treated waste water from the WWTP Eggenstein–Leopoldshafen. The sediment had a low organic content of 0.04 mg C/g with a grain size of 0.2–2 mm. Every 2 weeks the reservoir bottles containing raw waste water or effluent of the WWTP, respectively, were renewed. The reservoir

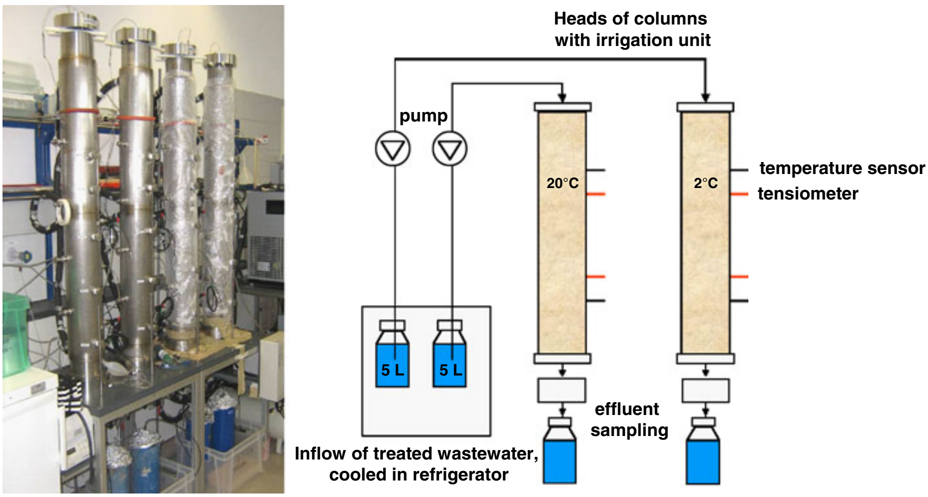

Fig. 1 Laboratory setup and scheme of the column experiment

bottles were stored in a refrigerator at 2°C. Hydraulic retention time in the columns was 6–7 days. By comparing leachate concentrations of the two biologically inhibited (cooled down to 2°C) and the two bioactive columns (20°C), biodegradation of the trace organics during soil passage was assessed. Temperature and water content in the columns were controlled by temperature sensors and tensiometers (Fig. 1). Five micrograms per liter of each substance were spiked into the reservoir bottles.

3 Results and Discussion

3.1 Screening of Emerging Pollutants

In total 29 different compounds out of a list of more than 50 target analytes were detected, including analgesics, an antiepileptic, lipid lowering agents, betablockers, steroid hormones, alkylphenols and trialkylphosphates. Minimum, maximum and median concentrations of the most frequently detected substances among pharmaceuticals in Jordan are presented in Table 1. Comparison with literature data shows that the detected values for pharmaceuticals in Jordan are in the same range as in Europe and the USA. As can be deduced from the data in Table 1, carbamazepine and the X-ray contrast agents diatrizoic acid and iopromide are among the more persistent compounds that also were found in groundwater (GW) with up to 180 and 940 ng/L for carbamazepine and diatrizoic acid, respectively, while iopromide was found once with 1,600 ng/L. These findings are in accordance with previously published studies on the persistence of these substances during waste water treatment and in the environment (Sacher et al. 2001; Clara et al. 2004; Joss et al. 2006). On the other hand, higher removal rates during waste water treatment have been reported for ibuprofen, naproxen, and bezafibrate (Zwiener et al. 2000; Quintana et al. 2005), which were not detected in the groundwater samples of this sampling campaign but still with up to 1,400, 550 and 390 ng/L, respectively, in surface water samples.

3.2 Elimination of Emerging Pollutants in Batch and Column Studies

Comparison of the removal of pharmaceuticals during a 12 weeks batch experiment with influent and effluent from a waste water treatment plant shows better removal efficiency in the effluent batch assay. Figure 2 depicts four of the substances investigated. Carbamazepine and diatrizoic acid (Table 2) were not removed in any of the assays. The increase of carbamazepine during the experiment is probably due to the conversion of carbamazepine glucuronide conjugates to the parent compound as it has been reported in literature (Vieno et al. 2007). Naproxen was completely removed in the batch assays with treated waste water (Table 2). However it showed no removal in one of the two active batch assays with untreated waste water. In contrast bezafibrate, diclofenac, and ibuprofen proved to be biodegradable in all assays. Slower biodegradation of the emerging pollutants in raw waste water might be due to competition with easily degradable organic matter present in the samples. Thus the DOC decreased by more than 50% from 46 to 20 mg/L in the two batches set up with raw waste water, while it varied between 7 and 8 mg/L in the batches with treated waste water. Nitrification was observed in both the raw and treated waste water batch assays.

Table 1 Minimum, maximum and median concentrations of selected pharmaceuticals in the Lower Jordan Valley compared with literature data from Europe and the USA

Group	Substance	Min/Max concentration (Median)			Literature[a]
		GW	SW	WW	[ng/L]
		[ng/L]	[ng/L]	[ng/L]	
		LOD 20 ng/L	LOD 20 ng/L	LOD 50 ng/L	
Lipid regulators	Gemfibrozil	<LOD/70 (<LOD)	<LOD/2100 (150)	<LOD/4800 (1400)	(SW) 840–4760, (b)
	Bezafibrate	<LOD	<LOD/390 (23)	<LOD/430 (270)	(SW) 130, (c)
Antiepileptic	Carbamazepine	<LOD/180 (<LOD)	<LOD/1600 (240)	<LOD/3600 (1800)	(GW) max. 900, (a) (SW) 870–6,300, (b)
Antiphlogistics	Naproxen	<LOD	<LOD/550 (<LOD)	<LOD/240 (<LOD)	(SW) max. 32, (d)
	Ibuprofen	<LOD	<LOD/1400 (<LOD)	<LOD/750 (140)	(SW) 1,000, (e) (WW) 230–6,400, (f)
	Diclofenac	<LOD	<LOD/160 (<LOD)	<LOD/390 (<LOD)	(SW) 680–5,450, (b)
X-ray contrast agents	Iopromide	<LOD/1600 (<LOD)	<LOD/3000 (660)	<LOD/2200 (190)	(SW) 8,100, (g)
	Diatrizoic acid	<LOD/940 (99)	<LOD/170 (<LOD)	<LOD/110 (<LOD)	(GW) 1,100, (a)
	Total number of samples	14	19	5	

GW groundwater, *SW* surface water, *WW* waste water

[a]Literature data represent mean values, if not marked otherwise (max. = maximum values); *a* Sacher et al. (2001), *b* Andreozzi et al. (2003), *c* Möder et al. (2007), *d* Benotti et al. (2009), *e* Kolpin et al. (2002), *f* Ternes (1998), *g* Ternes and Hirsch (2000)

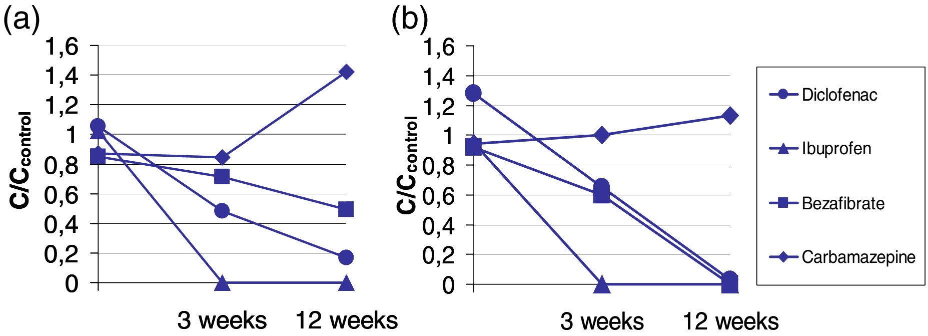

Fig. 2 Biodegradation of four pharmaceuticals during the batch experiments with filtered raw waste water (**a**) and effluent from a waste water treatment plant (**b**)

Elimination of pharmaceutical residues also has been investigated during soil passage in columns operated at 2°C and 20°C. The results demonstrate good reproducibility over time (Fig. 3). Complete elimination of diclofenac, bezafibrate, and naproxen was observed at 20°C whereas significantly less pronounced removal occurred at 2°C. The temperature controlled difference in elimination rates clearly indicated biological degradation of these compounds at room temperature. Carbamazepine and diatrizoic acid showed moderate to no removal, respectively, at 2°C and 20°C. However ibuprofen was completely eliminated even at 2°C.

Taking the log K_{OW} values of ibuprofen (3.5), diclofenac (4.51) and bezafibrate (4.25) into account (Scheytt et al. 2006; Meylan and Howard 1995), a better elimination of diclofenac and bezafibrate would have been expected, if sorption was the main elimination process. Therefore the column experiment indicates that ibuprofen is also biologically degraded at low temperature. However, in another column study conducted by Scheytt et al. (2007), significant retardation and less biotransformation for ibuprofen were reported. A short overview of previously published data on the six pharmaceuticals is presented in Table 2.

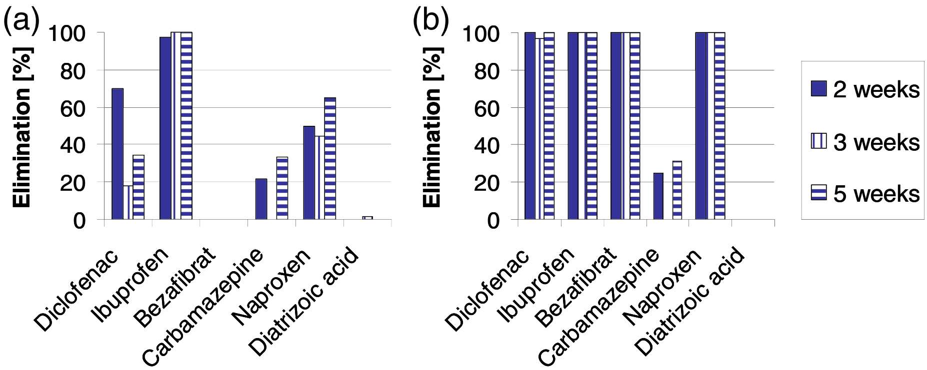

Fig. 3 Elimination of pharmaceuticals in flow-through soil columns at 2°C (**a**) and 20°C (**b**)

Table 2 Elimination of selected pharmaceuticals in this study compared to literature data

Substance	Elimination in this study		Elimination in literature	
	Batch (effluent)	Soil passage (20°)	Observed	Not observed
Bezafibrate	+ + +	+ + +	a, d	/
Carbamazepine	–	+	/	b, g
Naproxen	+ + +	+ + +	d, h	/
Ibuprofen	+ + +	+ + +	a, c, i	/
Diclofenac	+ + +	+ + +	e	a, d
Diatrizoic acid	–	–	f, j	a

– no removal, + removal <50%, ++ removal 50–90%, + + + removal >90%; *a* Joss et al. (2006), *b* Clara et al. (2004), *c* Zwiener et al. (2000), *d* Quintana et al. (2005), *e* González et al. (2006), *f* Drewes et al. (2001), *g* Scheytt et al. (2006), *h* Kimura et al. (2007), *i* Smook et al. (2008), *j* Haiß and Kümmerer (2006)

Biological degradation of ibuprofen, bezafibrate, and naproxen was observed also in previous studies, but contradictory data exist for diclofenac. Also for diatrizoic acid which neither showed removal in the batch assays nor during soil passage in our study, contradictory results regarding its biodegradability have been reported. For carbamazepine no biodegradation was observed.

Obviously, removal rates of pharmaceutical compounds in WWTPs and in the environment vary significantly. For instance, in case of diclofenac in some WWTPs elimination rates of 50–90% appeared, whereas almost no removal was observed in other WWTPs (Joss et al. 2006). There is a lack of understanding with respect to the biodegradability of specific pollutant mixtures, the effect of concentration ratios, and the relevance of co-metabolic processes. On the other hand, persistent pollutants such as carbamazepine might be suitable compounds to be used as anthropogenic tracers (Clara et al. 2004; Wolf et al. 2009).

4 Conclusion

Emerging organic pollutants such as diclofenac, carbamazepine and diatrizoic acid, which are commonly detected in European and US waters, have been assessed in waste water, surface water, and groundwater in the Lower Jordan Valley. The compounds and concentrations detected were in the same order of magnitude as reported for Europe and the USA. However, intensive water reuse in arid regions as well as water recycling strategies under moderate climatic conditions can result in an accumulation of persistent emerging pollutants. Therefore elimination processes should be improved. More studies into biodegradation efficiency as a function of waste water composition (metabolic/co-metabolic processes) and redox conditions (aerobic/anaerobic processes) are encouraged in order to develop sustainable treatment schemes for waste water reuse and groundwater recharge.

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