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Sources and processes affecting the spatio-temporal distribution of pharmaceuticals and X-ray contrast media in the water resources of the Lower Jordan Valley, Jordan

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ABSTRACT

The closed basin of the Lower Jordan Valley with the Dead Sea as final sink features high evapotranspiration rates and almost complete reuse of treated wastewater for irrigation farming. This study focuses on the water transfer schemes and the presence, spreading, and potential accumulation of pharmaceutical residues in the local water resources based on findings of a five-year monitoring program. Overall 16 pharmaceuticals and 9 iodinated X-ray contrast media were monitored in groundwater, surface water, and treated wastewater. A total of 95 samples were taken to cover all geographical settings and flow paths from origin (wastewater) to target (groundwater). Nine substances were detected in groundwater, with concentrations ranging between 11 ng/L and 33,000 ng/L. Sometimes, detection rates were higher than in comparable studies: Diatrizoic acid 75%, iopamidol 42%, iopromide 19%, iomeprol 11%, carbamazepine and iohexol 8%, ibuprofen 6%, and fenofibrate and iothalamic acid 3%. Concentrations in groundwater generally increase from north to south depending on the application of treated wastewater for irrigation. Almost all substances occurred most frequently and with highest concentrations in treated wastewater, followed by surface water and groundwater. As exception, diatrizoic acid was found more frequently in groundwater than in treated wastewater, with concentrations being similar. This indicates the persistence of diatrizoic acid with long residence times in local groundwater systems, but may also reflect changing prescription patterns, which would be in accordance with increasing iopamidol findings and surveys at local hospitals. Trend analyses confirm this finding and indicate a high probability of increasing iopamidol concentrations, while other substances did not reveal any trends. However, no proof of evaporative enrichment could be found. The high spatial and temporal variability of the concentrations measured calls for further systematic studies to assess the long-term evolution of organic trace substances in this reuse setting.

1. Introduction

Pharmaceutical residues and metabolites were detected in all aquatic compartments in the last two decades. Their presence in aquatic environments worldwide as well as their degradation under variable conditions in laboratory studies and wastewater treatment plants (WWTPs) have been subjects of many studies so far. Extensive environmental screenings were conducted on groundwater (Sacher et al., 2001; Barnes et al., 2008; Loos et al., 2010; Teijon et al., 2010; Fram and Belitz, 2011; Cabeza et al., 2012; Wolf et al., 2012), surface water (Nakada et al., 2007; Sacher et al., 2008; Loos et al., 2009), and treated wastewater (Drewes et al., 2002; Andreozzi et al., 2003; Zwiener and Frimmel, 2003; Vieno et al., 2007; Matamoros et al., 2008; Loos et al., 2013; Du et al., 2014). Publications so far have focused on substances used in large quantities or on components suspected of being persistent (Schulte-Oehlmann et al., 2007), such as X-ray contrast media (ICM), which can be detected in surface water, groundwater, and drinking water all over the world, with the concentrations ranging from ng/L up to lower μg/L levels (Sacher et al., 2001; Cabeza et al., 2012; Wolf et al., 2012). Duirk et al. (2011) even detected iopamidol (IPA), iopromide (IPR), iohexol (IHE), and diatrizoic acid (DIA) in drinking water sources in the U.S. with IPA detection rates of 60% and concentrations of up to 2700 ng/L. Most ICM behave conservatively in the environment due to their hydrophilic character and their structural design (Drewes et al., 2001). They are resistant against biochemical degradation processes and do not adsorb to sewage sludge (Kalsch, 1999; Haiss and Kummerer, 2006). Originally designed as contrast agents for

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X-ray diagnosis, these substances were administered in high doses (up to 200 g/treatment) and excreted almost non-metabolized due to their inert character (Perez and Barcelo, 2007). Subsequently, the ICM pass WWTPs without any significant reduction, with typical effluent concentrations reaching up to the μg/L level (Ternes and Hirsch, 2000; Drewes et al., 2002; Carballa et al., 2004; Perez and Barcelo, 2007). Other studies classified selected ICM as suitable wastewater tracers, as removal rates for DIA (0%) and IPA (17%) are small compared to removal rates between 83 and 89% for IHE, IPR, and IME (Ternes et al., 2007). WWTP effluents are the major entrance pathway, other possible sources are leaking sewers, sewage sludge or animal manure (Jekel and Reemtsma, 2006). Some techniques like photocatalytic degradation (Doll and Frimmel, 2004), advanced oxidation, and reduction processes (Jeong et al., 2010), activated powdered carbon (Lipp et al., 2012; Margot et al., 2013) or reverse osmosis (Busetti et al., 2010) seem to be suitable tools for ICM removal. Nevertheless, they are not state of the art in (waste-)water treatment and might not always be affordable, especially for developing countries. In most cases, degradation of pharmaceutical substances generally depends on environmental conditions, e.g. redox conditions (Massmann et al., 2008).

Mean differences in influent and effluent concentrations during wastewater treatment are taken from literature, stating 0% for DIA, −1.1% for the ICM iothalamic acid (ITA), and 17.4% for IPA. IHE (59.6%), IME (73.5%), and IPR (78.1%) showed much higher rates. The antiepileptic carbamazepine (CBZ) showed a mean difference of −5.7%, and the analgesic ibuprofen (IBU) of 74.2% (Deblonde et al., 2011).

Although trace concentrations of pharmaceuticals and ICM are measured only, concerns exist with regard to long-term exposure to low doses or potential toxic effects of mixtures of different substances due to interaction or synergetic effects (Jekel and Reemtsma, 2006). Their uptake in plants (Herklotz et al., 2010) and aquatic organisms (Nakamura et al., 2008; Paterson and Metcalfe, 2008; Meredith-Williams et al., 2012) has already been verified. Negative effects of organic trace concentrations on different animals were reported, e.g. vulture disease due to the analgesic diclofenac (DIC) in India (Taggart et al., 2007), Pakistan (Oaks et al., 2004), and Africa (Naidoo et al., 2009), collapse of fish population (Kidd et al., 2007) or changes in the social behavior of European perch (*Perca fluviatilis*) due to psychotropic drugs (Brodin et al., 2013). The increased formation of genotoxic disinfection byproducts in chlorinated drinking water in the presence of X-ray contrast media (ICM) was found (Duirk et al., 2011).

For the Lower Jordan Valley (LJV), the occurrence of several organic trace substances, including pesticides, pharmaceuticals, and ICM, in different water sources was described previously by Tiehm et al. (2012), Tiehm et al. (2011), and Wolf et al. (2009). The removal efficiencies of three local WWTPs and the release concentrations of two hospitals in Amman were described for four pharmaceuticals by Alahmad and Alawi (2010).

Due to the huge amounts of treated wastewater used for irrigation in the LJV (Alfarra, 2010), a close relationship to the quality of groundwater is assumed, as this is a source known to introduce persistent pharmaceuticals into the groundwater (Ternes et al., 2007; Siemens et al., 2008; Chávez et al., 2011). A study of irrigation with treated wastewater in China revealed increased pharmaceutical concentrations in the soil (Chen et al., 2011). Increasing concentrations of the antiepileptic carbamazepine (CBZ) in soils and the groundwater underneath caused by irrigation with treated wastewater were also found in Tunisia (Fenet et al., 2012). Elevated concentrations of the ICM diatrizoic acid (DIA) in groundwater compared to surface water or treated wastewater (Wolf et al., 2009) led to the hypothesis of evaporative enrichment of persistent organic micropollutants in this area. Other authors observed elevated pharmaceutical concentrations in groundwater compared to surface water: A study in Berlin detected higher DIA concentrations in groundwater (4 μg/L) than in surface water (2 μg/L) after bank filtration of water from a river into which treated wastewater was discharged (Putschew et al., 2000). Monitoring the injection of treated wastewater into a confined aquifer close to Barcelona (Spain) showed 13.4% of iopamidol (IPA) (157 ng/L) and 6.9% of iopromide (IPR) (574 ng/L) in groundwater samples, while these substances could not be detected in the raw water or the WWTP effluent (Teijon et al., 2010).

Based on the previous findings, the aim of this study was to investigate groundwater quality dynamics of the LJV using pharmaceuticals as pollution indicators and in particular different ICM, the antiepileptic CBZ, and the analgesic ibuprofen (IBU). The following questions were to be answered:

- What substances occur in the different water types and which concentration levels do they reach? Are they suitable anthropogenic tracers?
- Are there spatio-temporal trends or characteristic distribution patterns regarding concentrations and occurrence?
- Can trends and distribution patterns be related to the administration or known persistence of pharmaceuticals and do findings match with local infrastructures for wastewater distribution in irrigated agriculture?
- Is there any proof of accumulation processes in the groundwater?

2. Materials and methods

2.1. Local introduction

The LJV is a closed river basin with its deepest point being the Dead Sea (416 m bsl) acting as a final sink for all surface water and groundwater flows. Precipitation ranges between 300 and 400 mm in the northern part, but drops to 100 to 200 mm in the southern part, just north of the Dead Sea (MWI, 2004). The average annual temperature ranges between 23 and 28 °C. The climate is classified to be arid to semi-arid (Hötzl, 2009). Potential evapotranspiration rates are calculated to reach 2600 mm/a. Natural groundwater recharge is low with a minimum annual safe yield of 15 to 20 MCM (MWI, 2004). As almost all water running towards the LJV is used in agriculture, irrigation is assumed to be the main source of recharge. To allow for extensive agriculture in the LJV despite water scarcity, huge amounts of water are transferred to this area (Fig. 1). Yet, groundwater levels have been declining since the mid 1990s due to pumping and overexploitation of aquifers (Hötzl, 2009). The water level of the Dead Sea is dropping with a rate of almost 1 m/a (Salameh and El-Naser, 2000).

The main share of irrigation water is transferred by the King Abdallah Channel (KAC), diverting water from the Yarmouk River, which is then mixed with water from the Sea of Galilee according to the peace treaty of 1994. Along the KAC, the water is pumped into agricultural development areas at several turnout stations and diverted to the farm units for irrigation. Additionally, many farmers operate their (mostly unregistered) private wells to supplement the allocated KAC water (Alfarra, 2010). Ponds are used to mix groundwater with the KAC share or store water from the KAC for later application. Along the flow path down the LJV to Deir Alla, water from several dams is led into the KAC, as a result of which its water quality decreases continuously (Alkhoury et al., 2010). These dams, in turn, intercept significant amounts of treated wastewater from the highland settlements, together with base flow and flash floods, thus introducing water of poorer quality into the KAC. The main input of treated wastewater enters halfway down the LJV by the King Talal Reservoir (KTR), where the wastewater of the capital Amman (1.9 Mio inhabitants, compared to 6.3 Mio inhabitants of Jordan) is impounded after treatment in the As Samra WWTP. These transfers are illustrated schematically in Fig. 2.

Just before the KAC receives the KTR, approximately 45 MCM/a of water are pumped towards Amman, where it is treated to reach drinking water quality. After the inflow of the KTR into the KAC, the proportion of treated wastewater in the channel ranges between 50 and 70%