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Occurrence and distribution of psychoactive compounds and their metabolites in the urban water cycle of Berlin (Germany)

Ulrike Hass [a,b,*], *Uwe Duennbier* [b], *Gudrun Massmann* [c]

[a] *Institute of Geological Sciences, Freie Universitaet Berlin, Malteserstr. 74-100, 12249 Berlin, Germany*
[b] *Department of Laboratories, Berliner Wasserbetriebe, Motardstr. 35, 13629 Berlin, Germany*
[c] *Department of Biology and Environmental Sciences, Carl von Ossietzky Universitaet, Ammerlaender Heerstrasse 114-118, 26129 Oldenburg, Germany*

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ABSTRACT

The occurrence and distribution of six psychoactive compounds (primidone, phenobarbital, oxazepam, diazepam, meprobamate, and pyrithyldione) and a metabolite of primidone (phenylethylmalonamide) were investigated in wastewater treatment plant (WWTP) effluents, surface water, groundwater of a bank filtration site, raw and final drinking water, and in groundwater affected by former sewage irrigation.

Primidone and its metabolite phenylethylmalonamide were found to be ubiquitous in environmental water samples in Berlin. Maximum concentrations of 0.87 and 0.42 μg/L, respectively, were encountered in WWTP effluents. Both compounds are apparently not removed when passaging through the different compartments of the water cycle and concentrations are only reduced by dilution. Phenobarbital was present at nearly every stage of the Berlin water cycle with the exception of raw and final drinking water. The highest concentrations of phenobarbital (up to 0.96 μg/L) were measured in groundwater influenced by former sewage irrigation. Oxazepam was only present in WWTP effluents and surface waters (up to 0.18 μg/L), while diazepam was not detected in any matrix. Due to their withdrawal from the German market years ago, the pharmaceuticals meprobamate and pyrithyldione were only found in sewage farm groundwater (up to 0.50 and 0.04 μg/L, respectively) and, in case of meprobamate, also in decade old bank filtrate (0.03 μg/L).

Our results indicate a high persistence of some of the investigated compounds in the aquatic system. As a consequence, these pollutants may potentially reach drinking water resources via bank filtration if present in WWTP effluents and/or surface waters in partly closed water cycles such as Berlin's.

1. Introduction

The occurrence of pharmaceuticals from various prescription classes (such as analgesics, antibiotics, beta blockers, iodinated contrast media, and anticonvulsants) in the aquatic environment has been reported frequently in recent years (e.g., Ternes, 1998; Kuemmerer, 2001; Drewes et al., 2003; Schneider, 2004; Schwarzenbach et al., 2006; Vanderford and Snyder, 2006). The main source of organic trace pollutants in aquatic systems is wastewater treatment plant (WWTP)

* *Corresponding author*. Institute of Geological Sciences, Freie Universitaet Berlin, Malteserstr. 74-100, 12249 Berlin, Germany. Tel.: +49 30 8644 3360; fax: +49 30 8644 3339.
E-mail address: u.hass@gmx.net (U. Hass).
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effluent. Pharmaceutical residues may not be fully eliminated during sewage treatment and are thus discharged into receiving waters (Ternes, 1998; Heberer et al., 2002; Miehe, 2010). This is particularly problematic in urban areas with a partly closed water cycle such as Berlin (Germany), where drinking water production largely relies on groundwater recharge via bank filtration and/or artificial groundwater enrichment (Heberer and Stan, 1997; Heberer et al., 2004; Massmann et al., 2007). Bank filtration for drinking water production purposes is also common in other countries in Europe and in the USA (Ray et al., 2002). Moreover, especially in emerging countries suffering from high population growth and water scarcity at the same time, bank filtration will be increasingly used in the future to reclaim drinking water (e.g., India; Sandhu et al., 2011; Egypt; Shamrukh and Abdel-Wahab, 2008).

Besides the discharge of WWTP effluents to surface waters, the application of municipal wastewater on sewage irrigation farms may lead to considerable anthropogenic pollution of the environment, in particular of soils and groundwater (e.g., Scheytt et al., 2000; Richter et al., 2009; Hass et al., 2012). Irrigation of wastewater is still practiced in many countries of the world and was also common in Berlin until the 1980s (SenStadt, 2012). Although contaminants are diluted or partially removed through sorption and degradation in surface waters and during subsurface flow, they may still reach drinking water resources.

Previous studies by the authors revealed the presence of several psychoactive compounds in groundwater below a decommissioned sewage farm located within the catchment area of a drinking water treatment plant (DWTP) in Berlin (Hass et al., 2011, 2012). The antipsychotic drugs detected in those studies were further investigated in the current study and include primidone, its metabolites phenobarbital and phenylethylmalonamide, oxazepam, diazepam, meprobamate, and pyrithyldione.

Primidone is an anticonvulsant available on the market since the 1950s. In humans and animals, primidone is converted into two major pharmacologically active substances, phenobarbital and phenylethylmalonamide (El-Masri and Portier, 1998). While phenylethylmalonamide has no medical application, phenobarbital is also prescribed as an anticonvulsant. Moreover, phenobarbital is still one of the most widely used antiepileptic drugs worldwide (Kwan and Brodie, 2004). In the past, the barbiturate phenobarbital was predominantly used as a sedative and hypnotic. Introduced in 1912, phenobarbital was replaced in Germany in the 1960s by benzodiazepines for these indications due to an increased addiction potential and narrow therapeutic range (Linde, 1992). Two benzodiazepine derivative drugs, oxazepam and diazepam, are used extensively worldwide since the 1960s as tranquilizers for the treatment of anxiety and insomnia. Oxazepam is also an active metabolite of numerous benzodiazepines, including diazepam (Klotz, 1995). The anxiolytic drug meprobamate was introduced in 1955 but was soon (1960s) superseded by benzodiazepines (Mueller and Hartmann, 1995). Meprobamate is a non-prescribable narcotic in Germany (BtMAEndV, 1991) but is still available, for example, in other European countries and in the USA. Pyrithyldione is a sedative-hypnotic pharmaceutical introduced in 1949 (Linde, 1992). Due to adverse effects (Ibánez et al., 2000), pyrithyldione was withdrawn from the market in the 1980s.

Although some of these psychoactive compounds are no longer administered in Germany, they were detected in (decade-old) groundwater at concentrations up to 1 μg/L (Hass et al., 2012). Their presence in the environment raised concerns, initiating the present study exploring the occurrence and fate of these compounds in the entire water cycle of Berlin.

The objectives of this investigation were to: i) determine and monitor the occurrence of the described psychoactive compounds in environmental water samples from Berlin, including WWTP effluents, surface water, bank filtrate, groundwater influenced by sewage irrigation, and raw and final drinking water; ii) study the elimination of these substances during bank filtration and drinking water treatment, and iii) evaluate the risk of contamination of drinking water. This study provides important information on the distribution and the fate of these contaminants in the aquatic environment. At comparable hydrologic settings, the study also gives an insight into the potential negative effects when water supply relies on the indirect reuse of wastewater via bank filtration.

To date, the occurrence and fate of primidone in the environment has been described by several authors (e.g., Heberer et al., 2002; Drewes et al., 2003; Reddersen, 2004; Schneider, 2004; Hummel et al., 2006; Massmann et al., 2007; Guo and Krasner, 2009). Studies describing oxazepam and diazepam in the aquatic environment have also been published (e.g., Reddersen, 2004; Schneider, 2004; Hummel et al., 2006; González Alonso et al., 2010). However, to the best of our knowledge, a comprehensive overview of their behavior in the various stages of an urban water cycle is still lacking. Phenobarbital, phenylethylmalonamide, and meprobamate have rarely been investigated in aquatic environments in Germany and, thus far, no reports exist on the occurrence of pyrithyldione.

2. The Berlin water cycle

The drinking water supply for the 3.5 million inhabitants of Berlin is comprised completely of groundwater that mainly originates from induced bank filtration (60–70%) (Massmann et al., 2007; Moeller and Burgschweiger, 2008). Owing to the fact that the present hydrologic system can be regarded as semi-closed, Berlin's water production is partially based on the indirect reuse of wastewater (Ziegler, 2001; Massmann et al., 2004).

In the past (1876–1980s) (SenStadt, 2012), untreated wastewater was directly applied to sewage farms located within the city boundaries or in the close surroundings of Berlin (Fig. 1). These sewage fields were inundated over several decades with high amounts of wastewater and hence accumulated high contaminant loads so that today these fields have to be considered as legacy pollution sites. In a partially closed water cycle such as Berlin's, these sites pose a potential risk for surface and groundwater contamination. Increasing wastewater volume necessitated a reconsideration of wastewater disposal and led to the construction of large-scale WWTPs. Nowadays, household and industrial