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Fate and removal of polycyclic musks, UV filters and biocides during wastewater treatment

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ABSTRACT

The fate of polycyclic musks (PCMs) (HHCB, AHTN, ADBI, AHDI, ATII, DPMI), UV filters (3-(4-methylbenzylidene) camphor, 4-MBC; octyl-methoxycinnamate, OMC; octocrylene, OC; octyl-triazone, OT) and biocides (permethrin, carbendazim) during wastewater treatment was studied on a full-scale plant. Average influent concentrations of OMC, HHCB, OC, AHTN, 4-MBC and OT were at 20070, 4420, 1680, 1430, 960 and 720 ng L^{-1}, respectively. The other PCMs, permethrin and carbendazim ranged between < limits of quantification and 670 ng L^{-1}. Concentrations in the water line decreased significantly for most compounds. Removal rates for PCMs ranged from 72% to 86%, for UV filters from 92% to >99% and were at 92% and 37% for permethrin and carbendazim, respectively. Removal during wastewater treatment was mainly driven by sorption onto solids and biodegradation. For anaerobic sludge digestion, elimination of PCMs, OMC and the biocides was observed.

1. Introduction

Increasing interest has been addressed to personal care products and biocides in recent years. They have been detected in water systems where they can have adverse effects on aquatic ecosystems. The present study focuses on prominent organic compounds incorporated in these products: polycyclic musks (PCMs), UV filters, permethrin and carbendazim. PCMs (HHCB, AHTN, ADBI, AHDI, ATII, DPMI; Table 1) are widely used as fragrance ingredients in washing and cleaning agents, personal care products and in other consumables (Kupper et al., 2004). In 2000, the European production of the two most important compounds HHCB and AHTN was 1427 and 358 t, respectively, whilst commercialized volumes of the other PCMs were below 20 t (Anonymous, 2004). Due to high consumption volumes and low degradability, they have been detected in treated wastewater, in surface waters, in fish and in sediments (Bester, 2004, 2005; Heim et al., 2004; Schmid et al., 2004). Recently, antiestrogenic effects of HHCB and AHTN have been observed in an in vivo fish assay (Schreurs et al., 2004).

Organic UV filters are used in sunscreen products. The consumption is increasing due to the growing awareness of hazards posed by UV radiation and recommendations for prevention of skin cancer. To improve product stability, UV filters are used as additives for cosmetics, plastics, clothing or varnish (Ash and Ash, 2000; Balk et al., 2001). In Switzerland, 3-(4-methylbenzylidene) camphor (4-MBC), octyl-methoxycinnamate (OMC), octocrylene (OC) and octyl-triazone (OT) are among the most common compounds incorporated in sunscreen products (Poiger et al., 2004; Table 1). They absorb UV light in the wavelength range of 280–315 nm (UVB radiation). Concentrations in products can reach 10% and estimated volumes used in Switzerland are between 1 and 32 t for these compounds (Plagellat et al., 2006). UV filters have been detected in fish, lake water, wastewater (Poiger et al.,

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Table 1 – Selected compounds (further information is given in the supplementary Data)

Name and abbreviation used in the text		CAS
Polycyclic musks (PCMs)		
Galaxolide	HHCB	1222-05-5
Tonalide	AHTN	1506-02-1
Celestolide	ADBI	13171-00-1
Phantolide	AHDI	15323-35-0
Traseolide	ATII	68140-48-7
Cashmeran	DPMI	33704-61-9
UV filters		
3-(4-methylbenzylidene) camphor	4-MBC	36861-47-9
Octyl-methoxycinnamate	OMC	5466-77-3
Octocrylene	OC	6197-30-4
Octyl-triazone	OT	88122-99-0
Biocides		
Permethrin	Per	52645-53-1
Carbendazim	Car	10605-21-7

2004; Balmer et al., 2005) and in sewage sludge (Plagellat et al., 2006). This reveals concerns since some compounds are considered as endocrine active chemicals (Schlumpf et al., 2004).

Permethrin, a pyrethroid insecticide, is mainly used as wood preservative, veterinary and human pediculicide and for field pest control (Baser et al., 2003). Carbendazim belongs to the most used biocides for film preservation (Lindner, 2004) and is an important systemic fungicide for the production of field crops, fruit and vegetable. Analyses of sewage sludge have shown that permethrin and carbendazim occur in urban water systems (Plagellat et al., 2004). They are toxic to aquatic organisms in the ppb range (Cuppen et al., 2000; Baser et al., 2003; Gonzalez-Doncel et al., 2003). Tyler et al. (2000) have reported that environmental degradation of pyrethroid insecticides resulted in endocrine active metabolites.

Activities such as cleaning, washing of textiles, personal care or material protection may generate the release of hazardous chemicals incorporated in products into wastewater. UV filters and biocides in plastics, coatings or textiles may leach or volatilize from the matrix (Plagellat et al., 2006; Schoknecht et al., 2003) and end up in the sewer system with surface runoff. The transport through urban drainage systems and wastewater treatment plants (WWTPs) to the receiving waters is an important pathway for contamination of the aquatic environment. It is essential to know to which extent these compounds are removed in wastewater treatment and which mechanisms are responsible for removal. These issues have been studied on full-scale plants for certain PCMs. Results were obtained for biological treatment of different plant types (Joss et al., 2005) or in terms of a global input–output balance (Bester, 2004). Investigations on UV filters and biocides are not available. The aim of the present study was therefore to examine the fate and the removal of all PCMs which are actually in use (HHCB, AHTN, ADBI, AHDI, ATII, DPMI), UV filters (4-MBC, OMC, OC, OT) and biocides (permethrin, carbendazim) for different wastewater treatment steps and for the sludge line of a full-scale WWTP. A mass balance over a week was established for primary and biological water treatment and the sludge line. Additionally, sorption coefficients K_d for raw and secondary sludge were calculated.

2. Materials and methods

2.1. Sampling

Samples were obtained from WWTP Mittleres Emmental, Hasle, Switzerland, where a conventional activated sludge wastewater treatment is run. It serves a population of 23,000 from 17 mainly rural communities which comprise residential areas as well as industry and craft industry. The catchment area is drained by a combined sewer. At dry weather conditions, domestic and industrial sewage account for 44% and 16%, and infiltration water for 40%, respectively, of the influent volume. The mechanical treatment comprises a screen (16 mm), an aerated grit removal tank and a primary clarifier (residence time: 3 ± 0.3 h). The primary effluent flows through an aeration tank and a secondary clarifier with a return sludge to influent ratio of 1.4:1 and a combined residence time of 8 ± 0.9 h. The excess sludge is directed to the influent before the screen (Fig. 1). The solid retention time reaches about 16 days. Nitrogen is removed by nitrification and partial denitrification. Phosphorus removal is achieved by simultaneous precipitation using $FeClSO_4$. The sludge line comprises three thickeners (residence time: 2 days), a disinfection unit (pasteurization), a two-stage mesophilic anaerobic stabilization (average temperature: 34 °C; residence time: 20 days) and two storage tanks. The supernatants are decanted in the thickeners and the storage tanks and introduced into the influent and the primary clarifier, respectively.

Samples of 24-h flow proportional composites of influent, primary and secondary effluent were collected over 7 days in April 2002 using automated samplers. Sampling was performed at dry weather conditions (average daily inflow: $8000\pm800\,m^3$). Water and sludge flows were recorded (Fig. 1, Supplementary Data). Aliquots of supernatants from the thickener and the sludge storage tank were taken regularly during their transfer to the water line. Several times during the day, aliquots of excess sludge were obtained from the transfer pipe of return sludge. Aliquots of raw sludge from the thickener and from the storage tank were collected after removal of the supernatants in April and November 2002 as described by Kupper et al. (2004). Sludge and supernatants composite samples were prepared from at least eight aliquots. Samples were frozen within 1 day after sampling and stored at −20 °C until analysis.

2.2. Analytical methods

2.2.1. Chemicals and materials

HHCB (74% purity), AHTN (98%), ADBI (98%), AHDI (94.5%), ATII (90%) and DPMI (90%) were purchased from Promochem GmbH (Wesel, Germany). Quantification standards were prepared in isooctane at the following concentrations: for