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Retrospective study of triclosan and methyl-triclosan residues in fish and suspended particulate matter: Results from the German Environmental Specimen Bank

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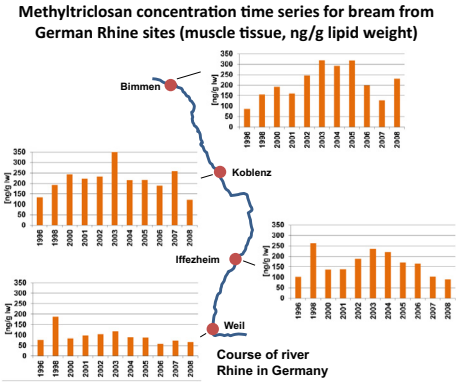
HIGHLIGHTS

- Triclosan and its transformation product methyl-triclosan were investigated in fish.
- Methyl-triclosan was found at higher concentrations than its parent compound.
- Levels of methyl-triclosan fish residues peaked between 2003 and 2005.
- Recently lower residues may be a result of a voluntary renunciation of triclosan use.
- Methyl-triclosan concentrations presumably pose no risk to aquatic organisms.

GRAPHICAL ABSTRACT



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ABSTRACT

A retrospective monitoring of triclosan (TCS; period 1994–2003 and 2008) and its potential transformation product methyl-triclosan (MTCS; period 1994–2008) was performed using archived fish samples from German rivers (16 sites, including Elbe and Rhine). At four of these sites suspended particulate matter (SPM) was also investigated covering the period 2005–2007. Samples were analyzed by GC/MS, either directly (MTCS) or after derivatization (TCS). TCS burdens of fish muscle tissue ranged from <0.2–3.4 ng g^{-1} ww (wet weight; corresponding to <2–69 ng g^{-1} lw, lipid weight) without apparent concentration trends over time. MTCS was detected at considerably higher concentrations in fish ranging from 1.0–33 ng g^{-1} ww (47–1010 ng g^{-1} lw) and increased until about 2003–2005. Thereafter, concentrations generally were lower, although at some sites single higher values were observed in recent years. In SPM, decreasing MTCS concentrations in the range 1–4 ng g^{-1} dry weight were detected while TCS was always below the limit of quantification. Assuming that MTCS concentrations are correlated to TCS consumption, the observed decrease in MTCS levels may be partly a result of the voluntary renunciation of TCS use in detergents for, e.g., laundry or dishwashing declared by a manufacturers' association in 2001. Because of a lack of ecotoxicity studies for MTCS, a QSAR-derived predicted no effect concentration (PNEC) was compared to averaged ambient water concentrations of fish which were calculated from

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maximum tissue residues by applying an appropriate bioconcentration factor from literature. Since these calculated water concentrations were below the PNEC it is assumed that MTCS alone poses no immediate risk to aquatic organism. The conversion to a PNEC for SPM organisms and comparison with detected SPM levels of MTCS also revealed no risk.

1. Introduction

Triclosan (5-chloro-2-(2,4-dichlorphenoxy)phenol, CAS No. 3380-34-5, short TCS) is a widely used antimicrobial agent. In the European Union (EU) TCS is regulated by the Biocidal Product Directive 98/8/EC and currently in the review program for 'existing substances' for authorization for several biocidal product types (e.g., as disinfectant or as preservative for materials). TCS is constituent of many personal care products (PCPs; also referred to as cosmetic products or cosmetics in the EU) like liquid soaps, deodorants, toothpastes and creams, and is also used for the impregnation of textiles to reduce microbial growth on these materials. During production and use (e.g., of TCS containing disinfectants or washing of impregnated textiles) TCS is emitted into wastewaters. In wastewater treatment plants (WWTPs) the vast majority of TCS is eliminated by biodegradation and adsorption to sewage sludge (Singer et al., 2002; McAvoy et al., 2002; Bester, 2003; Heidler and Halden, 2008). A minor amount, however, can still be detected in WWTP effluents. Furthermore, the TCS metabolite methyl-triclosan (2,4-dichloro-1-(4-chloro-2-methoxyphenoxy)benzene, CAS No. 4640-01-1, short MTCS) can be found in the effluents. MTCS is suspected to be a result of microbial methylation, e.g., during the water treatment process (Lindström et al., 2002) and may be applied as chemical marker for lipophilic WWTP-derived contaminants (Buser et al., 2006). The application of sewage sludge on land and subsequent run-off into aquatic systems is a further potential source of TCS and MTCS to the environment, although the run-off potential for TCS seems to be low (Sabourin et al., 2009).

TCS is highly toxic to bacteria and phytoplankton and toxic to many other aquatic organisms (Schweizer, 2001; Orvos et al., 2002; DeLorenzo et al., 2008). Its environmental half-life, however, is assumed to be relatively low as it is susceptible to photo- and biodegradation (Lindström et al., 2002; Reiss et al., 2002). The transformation product MTCS is more persistent under environmental conditions (Lindström et al., 2002; Balmer et al., 2004), but little is known about its ecotoxicity (Balmer et al., 2004; Stevens et al., 2009; Lyndall et al., 2010; Brausch and Rand, 2011). Both compounds have a logarithmic octanol/water partition coefficient (log K_{ow}) of greater than 3 (TCS: 4.7, MTCS: 5.2; estimated with EPI Suite, EPA, 2008) and are thus potentially bioaccumulative (e.g., according to the criteria discussed in Gobas et al., 2009).

Triclosan is suggested as one of the substances of possible concern on the new EU watch list for monitoring of surface waters in the context of the Water Framework Directive (WFD). By gathering monitoring data on these compounds the European Commission intends to break the vicious circle of the necessity of monitoring substances in order to regulate them, and of regulating substances in order to monitor them (European Parliament, 2012).

An environmental risk assessment by the international Association for Soaps, Detergents and Maintenance Products came to the result that the total input of TCS into the environment should not be increased. Based on this outcome, the German Cosmetic, Toiletry, Perfumery and Detergent Association (IKW) recommended to their member companies in 2001 to voluntarily refrain from using TCS in new formulations of detergents and to substitute TCS in formulations of existing products (IKW, 2001).

In order to investigate the effectiveness of the renunciation a retrospective monitoring of TCS and MTCS in bream of six representative German rivers was performed using samples of the German Environmental Specimen Bank. The preliminary study, covering the years 1994–2003, revealed low TCS levels as well as strong regional differences in MTCS concentrations until 2003 (Boehmer et al., 2004; only wet weight data). The present study expands the MTCS time series to 2008, provides lipid-normalized concentration data, and thus allows a comprehensive overview of MTCS levels in fish from German rivers in the time period after the voluntary reduction measure (for the follow up TCS was only measured in 2008). In addition, suspended particulate matter (SPM) samples from the German ESB were investigated for TCS and MTCS loads. SPM may be regarded as equivalent to freshly deposited sediment. Thus, SPM monitoring data are an alternative to assess the potential risk of contaminants for sediment organisms (European Commission, 2010; Schubert et al., 2012).

2. Materials and methods

2.1. Environmental Specimen Bank sampling and sample treatment

Sampling and storage were performed according to the concept of the ESB (UBA, 2008) following detailed standard operating procedures. Bream (*Abramis brama*) is a non-predatory freshwater fish

Fig. 1. River sampling sites of the German ESB.