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Under the influence of regulations: spatio-temporal trends of the UV filter 2-Ethylhexyl-4-methoxycinnamate (EHMC) in German rivers

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Abstract

Background: Globally, 2-Ethylhexyl-4-methoxycinnamate (EHMC) is one of the most commonly used UV filters in sunscreen and personal care products. Due to its widespread usage, the occurrence of EHMC in the aquatic environment has frequently been documented. In the EU, EHMC is listed under the European Community Rolling Action Plan (CoRAP) as suspected to be persistent, bioaccumulative, and toxic (PBT) and as a potential endocrine disruptor. It was included in the first watch list under the Water Framework Directive (WFD) referring to a sediment PNEC of 200 µg/kg dry weight (dw). In the light of the ongoing substance evaluation to refine the environmental risk assessment, the objective of this study was to obtain spatio-temporal trends for EHMC in freshwater.

We analyzed samples of suspended particulate matter (SPM) retrieved from the German environmental specimen bank (ESB). The samples covered 13 sampling sites from major German rivers, including Rhine, Elbe, and Danube, and have been collected since mid-2000s.

Results: Our results show decreasing concentrations of EHMC in annual SPM samples during the studied period. In the mid-2000s, the levels for EHMC ranged between 3.3 and 72 ng/g dw. The highest burden could be found in the Rhine tributary Saar. In 2017, we observed a maximum concentration ten times lower (7.9 ng/g dw in samples from the Saar). In 62% of all samples taken in 2017, concentrations were even below the limit of quantification (LOQ) of 2.7 ng/g dw.

Conclusions: The results indicate a general declining discharge of EHMC into German rivers within the last 15 years and correspond to the market data. Although the measured levels are below the predicted no-effect level (PNEC) in sediment, further research should identify local and seasonal level of exposure, e.g., at highly frequented bathing waters especially in lakes. In addition, possible substitutes as well as their potentially synergistic effects together with other UV filters should be investigated.

Keywords: UV filter, EHMC, Environmental trend monitoring, Major German river basins, Suspended particulate matter, Water Framework Directive

Background

EHMC (2-Ethylhexyl-4-methoxycinnamate), also known as octinoxate, is one of the most popular organic UV filters used in sunscreens. EHMC as an isomer mixture consists mainly of more than 80% of the trans-isomer (2-Ethylhexyl trans-4-methoxycinnamate, EC no.: 629-661-9, CAS no.: 83834-59-7) and has been registered

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under REACH as 2-Ethylhexyl 4-methoxycinnamate before 2013 (EC no.: 226-775-7, CAS no.: 5466-77-3). Both isomers further include the R- and S-enantiomers. Therefore, EHMC may refer to a composition containing four constituents. As an UVB filter, EHMC is authorized by the European cosmetics regulation [1] for use in cosmetics up to 10%. In order to achieve complete protection against both UVB and UVA radiations, EHMC is commonly combined with other UV filters in sunscreen products according to the recommendations given by the European Commission in 2006 [2]. Apart from its application as a sunscreen, EHMC is increasingly used as an UV absorber to prevent a variety of personal care, washing and cleaning products against photodegradation [3, 4].

EHMC has a log $K_{OW} > 5.8$ [3, 5], so adsorbing to solids would be expected. Although the compound is slightly soluble in water [6], it has been widely detected in fresh and sea water up to 4043 ng/l [7–11]. A seasonal pattern with higher concentrations during the summer month was observed at beaching sites [12]. EHMC is lipophilic and accumulates in biota showing a tendency to bioaccumulate through different trophic levels [13].

The substance is not persistent in the environment as it is readily biodegradable and also degradable under anaerobic conditions. EHMC is unstable in sunlight and can be transformed from trans-EHMC to emergent cis-EHMC which showed a greater risk to genotoxic effects than the trans-isomer [14]. Endocrine-disrupting potential of EHMC has been suggested in several in vitro and in vivo studies [15–20]. In addition, thyroid-disrupting effects of EHMC are suggested in experimental studies [21–24]. EHMC has demonstrated multiple hormone activities in fish with gene expression profiling showing antiestrogenic activity [18]. Recently it has been reported that EHMC may affect reproduction and thyroid hormonal balance of fish [25].

The broad use in large amounts is associated with its occurrence in the environment and humans, which has raised significant concerns about the safety of EHMC. The concerns as regards environmental aspects are taken care under the REACH regulation, where EHMC is registered as the so-called existing substance supplied in the EU since decades at high tonnage between 1000 and 10,000 t/a. According to ECHA, the structural similar substances 2-Ethylhexyl trans-4-methoxycinnamate and 2-Ethylhexyl 4-methoxycinnamate may be jointly evaluated for environmental risks. EHMC has been included into the CoRAP list 2014 for further evaluation as suspected PBT and its potential for endocrine activity in amphibians and fish [26, 27]. As part of the evaluation, emissions will be assessed with regard to risk to the aquatic environment. On this basis, EHMC was placed on the European watch list of substances that may pose a significant risk to the aquatic environment [28]. Monitoring in sediment or SPM had been recommended for this lipophilic substance. In 2018, it was decided to remove EHMC from the watch list and to consider its re-inclusion to the third watch list. But again in 2020, EHMC has not be included into the revised surface water watch list due to concerns about EU-wide comparable sediment monitoring [29, 30].

The present study is part of a project in order to provide information of emerging contaminants, which are under regulatory pressure, e.g., plasticizers [31]. This paper aims to investigate spatial patterns and retrospective temporal trends of EHMC in freshwater systems and intends to support the watch list mechanism. We analyzed archived SPM samples from the German environmental specimen bank (ESB) for the mixture of cis- and trans-isomers. The samples were collected between the mid-2000s and 2017 from the major German river basins, like Rhine, Danube, Elbe, and their tributaries. Another purpose of this study was to evaluate whether EHMC levels in the environment were already affected by regulatory processes. For our best knowledge, this is the first long-term monitoring. Such retrospective monitoring with archived ESB samples allows trend assessment for EHMC.

Methods

Selection of samples from the ESB

Here we give a brief description of sample collection and preparation and the analytical method. Details can be found in the references cited and in Supporting Information (**SI**). The extensive sampling and archiving program of the ESB includes *inter alia* SPM sampling in large German Federal waterways. Since 2005, SPM samples are taken at nine sites in the Rhine (R1, R3, and R4) and Elbe (E1, E2, E4, and E5) river basins and the Elbe tributaries Saale (Sa) and Mulde (Mu). Two sites in the Saar (S1 and S2) and two sites in the Danube (D1 and D3) are sampled since 2006 and 2009, respectively [32]. A short characterization of the sampling sites is given in Additional File 1: Table S1 (adapted from [33]).

Suspended particles are collected in sedimentation boxes and sampled on a monthly basis. 12 monthly samples are than pooled to one annual sample. The samples are sieved (< 2 mm), homogenized, and freeze-dried [34].

In total, 73 samples were analyzed. For each site EHMC levels were determined for the first sampling year and for 2017. Time trends between 2005 (2006 for the Saar site) and 2017 were studied at eight sites (E1, E2, E4, Sa, R1, R3, R4, and S2) by analyzing samples from every second year of the annual ESB sampling program. Details on sampling frequency and the number of samples for each site are listed in Additional File 1: Table S2.

Chemicals and materials

EHMC was purchased from Sigma-Aldrich. EHMC has been analyzed together with other emerging substances, such as plasticizers and fragrances. In order to cover a broad retention range, four deuterated phthalates were used for quantification. One of them, d4-Dihexyl phthalate (d4-DHP) was selected as deuterated internal standard (IS) for EHMC analysis and was also purchased from Sigma-Aldrich. The suitability of d4-DHP for quantification of EHMC had been previously tested on the basis of chromatographic behavior, response factor, and similar behavior during the sample treatment process (recovery rates). Stock solutions and working solutions of EHMC and the labeled standard were prepared in acetonitrile and stored at 5 °C. Further information on chemicals and materials is available in **SI**. Chemical and physical properties of EHMC are described in Additional File 1: Table S3.

Extraction and clean-up

The method has already been presented [31] and is only briefly described here. Before extraction, the deuterated phthalate d4-DHP was added to the aliquots of the freeze-dried SPM sample. Extraction was performed in an ultrasonic bath using two times acetone/dichloromethane/n-hexane followed by an n-hexane/acetone mixture (each for 10 min). The combined extracts were concentrated to approximately 0.5 ml in a N_2 stream. Samples were cleaned up on a Florisil column with ethyl acetate/acetonitrile/dichloromethane. The eluate was concentrated in a N_2 stream to approximately 0.5 ml and reconstituted in acetonitrile for analysis. Details of the extraction and clean-up procedure are described in **SI**.

LC–MS/MS analysis

Analysis was performed by liquid chromatography—mass spectrometry analysis (LC–MS/MS), using an Agilent 1290 infinity II LC combined with an SCIEX QTRAP 6500 + MS. LC–MS/MS operation parameters are presented in **SI**. EHMC was quantified using d4-DHP as IS, which was added prior to extraction (for details see Additional File 1: Tables S4 and S5).

Quality assurance

Pretreatment of the laboratory tools to avoid contamination is described in **SI**. As mentioned above, the investigation of EHMC in SPM samples was part of a study including also plasticizers in the analyte spectrum. The analysis of plasticizers, especially of phthalates, is notorious for blank problems. Hence, the quality assurance procedures and standards were adapted to this problematic substance group. Method blanks were prepared to check possible contamination during the complete sample treatment. Additionally, a blank check of each clean-up column was carried out prior to use. Concentrations of the analyte in samples were quantified using d4-DHP as IS after the mean blank values (average value of a preparation sequence, $n = 4$–5) have been subtracted. The limit of detection (LOD) and the limit of quantification (LOQ) were estimated by measuring replicates ($n = 10$) of method blank values. LOD and LOQ were calculated by using the standard deviation (SD_{blank}) of the blanks ($LOD = 3 * SD_{blank}$ and $LOQ = 9 * SD_{blank}$). For EHMC the LOQ was 2.7 ng/g dw (the LOD value is given in **SI**). The validation of the analytical method for the UV filter was assessed through spikes of the analytes to aliquots (about 1 g) of a pooled SPM sample. The pooled SPM sample was obtained by mixing already extracted SPM samples, which were dried before pooling. The spiked samples followed the same procedure as the other samples in this study. Recovery rates of 94% and 104%, respectively, ($n = 5$ for each of the two concentration levels 102 ng/g dw and 255 ng/g dw investigated) were obtained with a relative standard deviation of about 2.4% (see Additional File 1: Table S7). The repeatability was calculated as the relative standard deviation (RSD) of five replicate measurements of the same SPM sample under repeatable conditions. RSD values were 5–25% for EHMC.

Statistical analyses

In multiple analyses of the same SPM sample ($n = 2$–5), a geometric mean value (GM) was determined from the individual values. Values below LOQ were taken into account with half of LOQ.

For trend analysis, a software tool from the German Environment Agency was applied (LOESS-Trend, Version 1.1, based on Microsoft Excel). This tool fits a locally weighted scatterplot smoother (LOESS; fixed window width of seven years) through the yearly contaminant levels and then tests for significance of linear and nonlinear trend components by means of an Analysis of Variance (ANOVA) [35].

Results and discussion

Spatial and temporal comparison of EHMC levels in riverine SPM in the mid-2000s and 2017

Figure 1 shows the levels of EHMC in SPM from six German rivers at sampling sites in the respective first year of sampling in 2005, 2006, and 2009 in comparison to the last investigation in 2017. Detection frequencies are given in **SI** (Additional File 1: Table S8a). We found

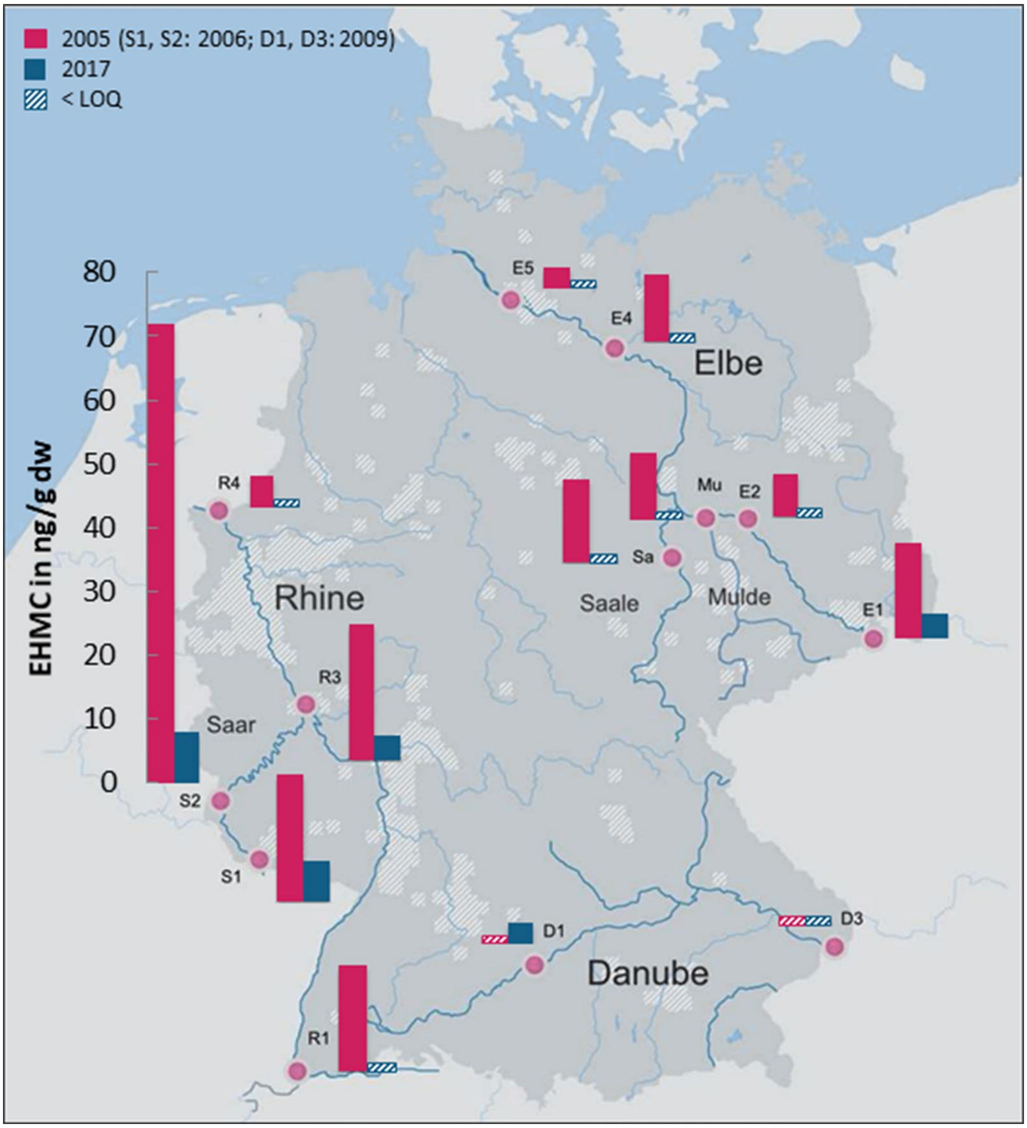

Fig. 1 EHMC in SPM samples from German rivers (concentration in ng/g dw). Measured value < LOQ of 2.7 ng/g dw has been set to half of LOQ

significant differences for EHMC between the individual locations. In the mid-2000s, at 11 sites in the rivers Rhine, Elbe, Saale, Mulde, and Saar, the EHMC concentrations ranged from 3.3 ng/g dw (E5, downstream Elbe) to 72 ng/g dw (S2, Saar), which is about a factor of 20. In 2017, the detection frequency (% ≥ LOD) for EHMC was 100% at these sites, but the levels had decreased significantly compared to 2005/06. The maximum level was also measured in the sample of the Saar river (S2, 7.9 ng/g dw), but was 10 times lower than it was in the mid-2000s. For the E1, R3, and S1 sites, the levels had decreased to 20–30% of the first measured value. At seven sites (E2, E4, E5, Mu, Sa, R1, and R4) we found concentrations below LOQ.

The EHMC concentrations at the Danube sites D1 and D3 were below LOQ in 2009 and at D3 in 2017. In the sample taken in 2017 from D1, a value of 3.3 ng/g dw was measured.

In order to reduce the inherent variability of SPM samples, concentrations have been normalized to the total organic carbon (TOC) content in the first year of sampling and in 2017 (TOC contents and normalized LOQs for the individual sites are given in Additional File 1: Table S6a-b; the normalized concentrations are listed

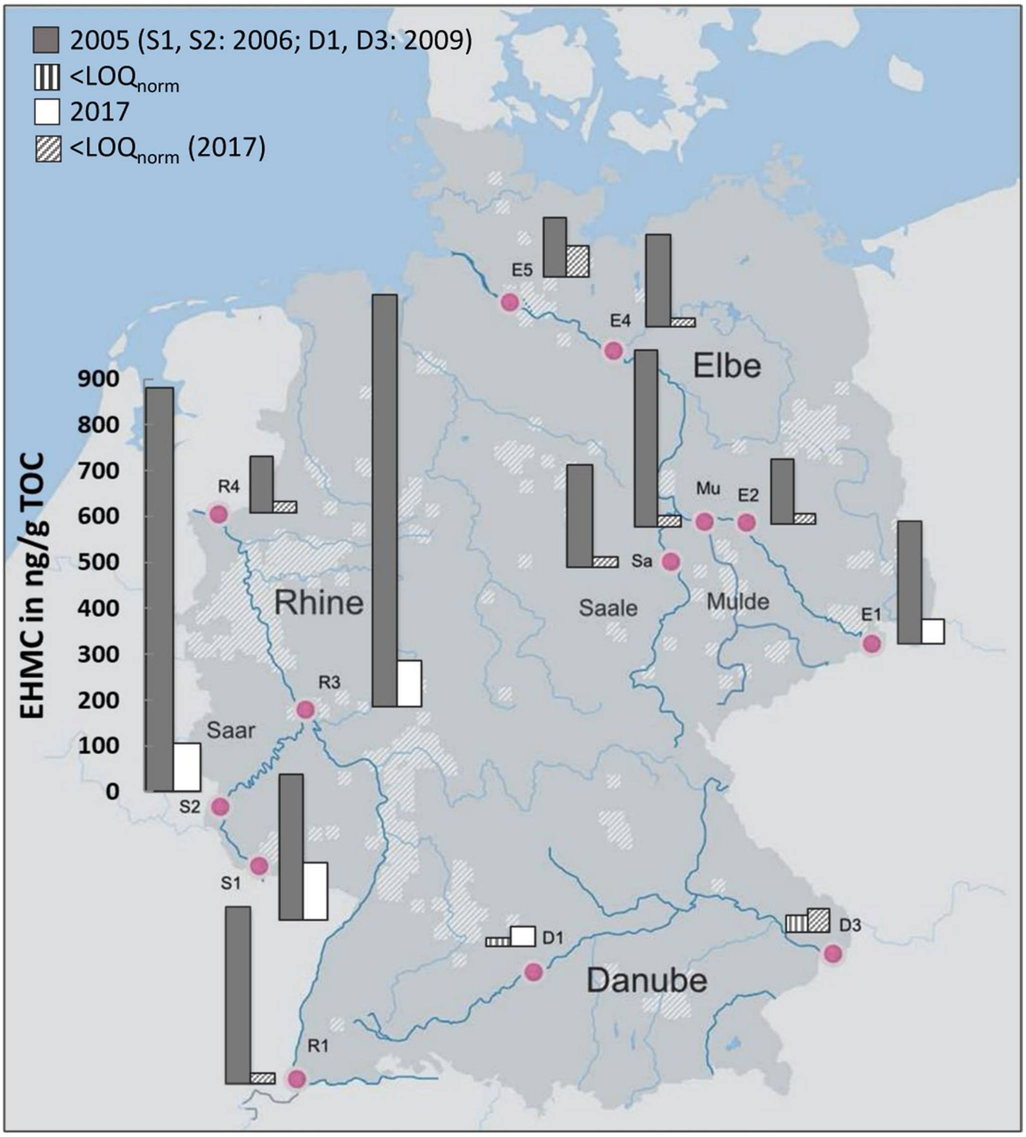

Fig. 2 EHMC concentrations in SPM samples from German rivers, normalized to TOC content (concentration in ng/g TOC). Measured value < LOQ$_{norm}$ has been set to half of < LOQ$_{norm}$

in Additional File 1: Table S8b). As shown in Fig. 2, the normalization underlines the high values in Rhine (R3, 891 ng/g TOC in 2005) and Saar (S2, 881 ng/g TOC in 2006). Although, there are smaller differences between the individual sites compared to the absolute values, a similar spatial and temporal pattern could be observed after normalization. An exception is the normalized concentration in R3 from 2005, which is about twice as high as in R1 (448 ng/g TOC). This is in contrast to the absolute values (R1, 17 ng/g dw; R3, 21 ng/g dw).

The Rhine is the river with the highest water discharge in Germany. Its average volume of water doubles between R1 and R3 from 1000 m^3/s to approximately 2000 m^3/s [36, 37], mainly due to the confluence of the major tributaries Main and Neckar. Despite the higher dilution potential, we found increasing EHMC levels between R1 and R3 in the mid-2000s and to a lesser extent in 2017. A major pollution source may be attributed to a production site of UV filters (including EHMC) located upstream of R3. Additionally, the discharge of Main and Neckar can contain more than 30% and 50%, respectively, of wastewater treatment plant effluents at their confluence with the Rhine [38]. From R3 downstream to R4, the EHMC level decreased and low concentrations were observed at the site R4 (2005: 5.0 ng/g dw and 2017: < LOQ). The TOC-normalized levels from 2005 underline the concentration pattern in the longitudinal profile of the Rhine (see Fig. 2).

Maximum values were detected in SPM samples from the two Saar sites, particularly at S2. This may be originated by urban impact. S2 is located downstream from the cities of Saarbrücken and Saarlouis. The water volume of Saar is low [39] and in the investigated river section, wastewater treatment plant effluents can reach up to 50% of the water discharge [38].

An impact of urban and industrial wastewater discharge on EHMC levels in surface water systems was also observed in other studies. Removal rates for EHMC in wastewater treatment plants reported in the literature ranged from 40 to 100% [8, 40–42]. Although the hydrophobic UV filter is mainly found in sewage sludge [43], EHMC has been detected in effluent water with contents up to 849 ng/l [44, 45], in effluent sediment [8] and directly downstream from the effluent point [46, 47]. Kameda et al. found in the sediment of heavily polluted rivers up to 30 ng EHMC/g dw, whereas only up to 8 ng/g dw were detectable in the sediment of background sites [8].

The EHMC levels found in this study are in line with those found in other investigations in sediment or SPM samples in Europe (see Table 1). The overall data indicate a decreasing contamination in European surface waters. Since the mid-2010s, mean and median values were mainly below LOQ. In contrast to previous studies, the frequency for EHMC values ≥ LOQ ranged between 0 and 38% and EHMC was only detected in low concentrations.

Temporal trends of EHMC

To identify temporal trends, SPM samples from eight sampling sites (E1, E2, E4, Sa, R1, R3, R4, and S2) were analyzed at intervals of one to two years (sampling interval see Additional File 1: Table S2). The temporal course of concentrations for EHMC in SPM from eight sampling sites between 2005 (2006 in S2) and 2017 are presented in Fig. 3a-h. EHMC levels decreased significantly ($p < 0.05$) in SPM samples from all sites, in particular before 2008.

For EHMC concentrations, Additional File 1: Fig. S1a shows the results of the linear trend analysis, given as the average annual decline. The results of the linear trend analysis based on TOC-normalized values are illustrated in Additional File 1: Fig. S1b.

The maximum decline rate was observed in samples from S2 with annual decreases of 5.2 ng/g dw and 62 ng/g TOC, respectively. At the sampling site with the highest TOC-normalized level in 2005 (R3), we found a lower rate of decrease of 40 ng/g TOC per annum.

Our findings are in accordance with the EU market data. For EHMC the frequency of use strongly decreased. In 1998, EHMC was an ingredient in more than 50% of the sunscreens investigated [11]. A study in Denmark in 2002 showed similar results (49%) [56]. Since the mid-2010s, shares of EHMC-containing sunscreen products of 1.5–17% were reported [57–61]. This development could be related to the fact that REACH has been adopted in 2006, whereupon, EHMC has been registered

Table 1 Overview on reported EHMC concentrations in European SPM samples and sediment (concentration unit: ng/g dw)

Sampling location	Sampling year	Matrix	LOQ	% ≥ LOQ	Range	Median	Mean	Study
Germany, main rivers and tributaries	2005/06	SPM	2.7	100	3.3–72	13	18	our study
Germany, lakes near Leipzig	2007	sediment	5[a]	100[b]	14–34	n.a[c]	n.a[c]	[48]
Spain, Ebro river basin	2009	sediment	5.3	15	< LOQ-42	< LOQ	6	[49]
Spain, Andulusian coast	2012	sediment	0.129	83	< LOQ-26.2	12.8	13.1	[50]
Norway, Oslofjord and Lake Mjøsa	2013	sediment	n.a[c]	100[b]	8–20	11	13	[51]
Sweden, Uppsala WWTP effluent, bathing lakes in South Sweden	2014	sediment	7	38	< LOQ-35	< LOQ	10	[46]
Spain, Catalan rivers	2014	SPM	6.5	0	< LOQ	< LOQ	< LOQ	[42]
Italy, Adriatic Sea	2014	sediment	0.129	100	0.7–10.4	2.9	3.3	[52]
Greece, Evrotas river	2014/15	sediment	0.2	0	< LOQ	< LOQ	< LOQ	[53]
Italy, Alpin rivers	2015	sediment	0.1	0	< LOQ	< LOQ	< LOQ	[54]
Germany, German Bight, Baltic Sea, Skagerrak and Kattegat	2015/17	sediment	0.25	7	< LOQ-0.32	< LOQ	< LOQ	[55]
Germany, main rivers and tributaries	2017	SPM	2.7	38	< LOQ-7.9	< LOQ	2.9	our study

[a] LOD (LOQ value is not reported)

[b] 100% ≥ LOD (information given by the reference)

[c] n.a, value not available

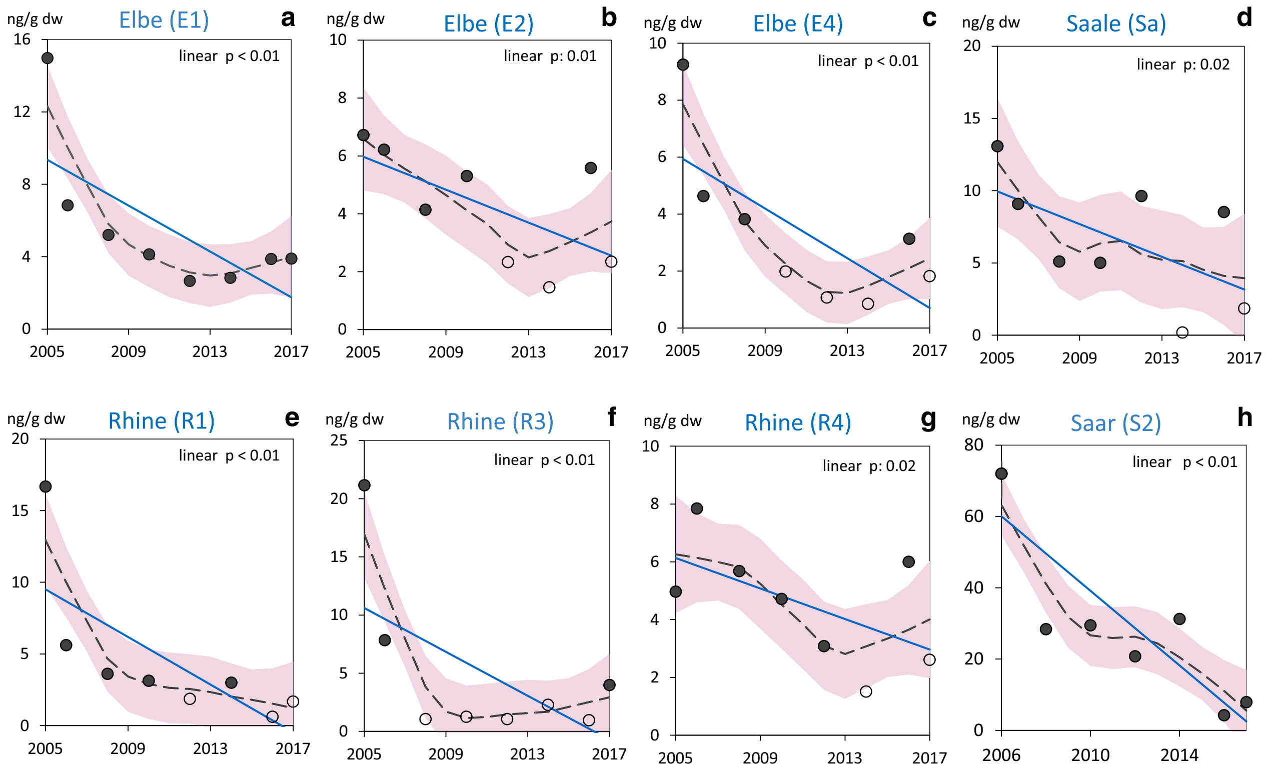

Fig. 3 **a**–**h** Temporal trends for EHMC in annual SPM samples from eight sampling sites. ● measured value (ng/g dw); ○ measured value < LOQ (ng/g dw); ––– LOESS Smoother; — linear trend

in 2010, evaluated in 2013, and listed on the CoRAP list in 2014 because of insufficient information on environmental risks. Furthermore, in the beginning of the 2000s, there was a growing awareness of additional damage caused by UVA radiation. As a consequence, UVA and broadband filter had been increasingly available on the EU market [62, 63].

Regulatory assessment of the exposure data

The concentrations found in time-integrated samples of suspended particulate matter give no rise of concern as all levels determined and especially the actual levels of less than 0.01 mg/kg dw are far below the PNEC in sediment of 0.2 mg/kg dw [28, 64]. This appears to indicate that EHMC contamination may not be of concern for the studied aquatic environment. We have to point out that the samples of suspended particulate matter represent annual average composites of monthly taken samples at equal proportions. Therefore, our study gives a general view on spatial and annual variations from a retrospective view and does not address possibly occurring local higher short-term concentrations.

Conclusions

Our study indicates a decreasing discharge of EHMC into German waters within the last 15 years. This might be attributed to a decreasing use as well as a changing usage pattern in conjunction with improved wastewater treatment. Although the frequency of use as an ingredient in sunscreens in Germany strongly decreased from about 65% in 1994 to 15% in 2014, EHMC is still one of the most important UVB filters in daily care products [58]. EHMC frequently occurs in lip or skin care products and face creams in about 30% up to 75% [57–59]. Therefore, indirect and continuous discharge in freshwater systems via urban wastewater cannot be excluded and might be related to the current levels in highly industrialized and densely populated areas. Our data in support of the ongoing environmental exposure assessment [65] underline the need of a targeted sediment monitoring and serve as a starting point for designing future monitoring programs. Thereby, possible occurrence and changing use patterns of EHMC should to be taken into account as required for the watch list monitoring. Nevertheless, the occurrence of possible substitutes, other UV filters and their potentially synergistically effects should be critically investigated in further studies. Among the new developments are the use of inorganic nanoparticles [66] and high-molecular weight compounds, like triazine derivatives [58]. Recent studies already documented the upcoming presence of Ethylhexyl triazone (EHT) and Bis-ethylhexyloxyphenol methoxyphenyl triazine (BEMT) in the aquatic environment [55, 67]. The growing demand of UV filters and current increases in production [68] may cause a higher pollution of water bodies with these novel compounds.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s12302-020-00448-w.

Additional File1: **Table S1** Sampling sites of the ESB. **Table S2** Sampling and measurement period between 2005 and 2017. **Table S3** General information on EHMC. **Table S4** Information on LC-MS/MS system and parameters. **Table S5** Information on substance specific parameters for EHMC detected by LC-MS/MS. **Table S6a** TOC contents in SPM samples at the sampling sites between 2005 and 2017 [6] (in µg/g). **Table S6b** LOQnorm values at the sampling sites between 2005 and 2017 (in ng/g TOC). **Table S7** Recoveries for EHMC at two different concentration levels. **Table S8a** Concentrations of EHMC in SPM samples at the sampling sites (in ng/g dw). **Table S8b** TOC-normalized concentrations of EHMC in SPM samples at the sampling sites (in ng/g TOC). **Fig S1** Average annual change in EHMC concentrations resp. in EHMC concentrations normalized to TOC between 2005 (resp. 2006 at S2) and 2017 (significant linear regression; $p < 0.05$) (PDF 408 KB)

Abbreviations

EHMC: 2-Ethylhexyl-4-methoxycinnamate; UV filter: Ultraviolet filter; EU: European Union; CoRAP: Community Rolling Action Plan; PBT: Persistent, bioaccumulative, and toxic; WFD: Water Framework Directive; dw: dry weight; SPM: Suspended particulate matter; ESB: German environmental specimen bank; LOQ: Limit of quantification; PNEC: Predicted no-effect concentration; d4-DHP: D4-Dihexyl phthalate; IS: Internal standard; LC–MS/MS: Liquid chromatography mass spectrometry analysis; LOD: Limit of detection; RSD: Relative standard deviation; GM: Geometric mean value; ANOVA: Analysis of Variance; TOC: Total organic carbon.

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Authors' contributions

RN was involved in the experiments. RN and AD designed the study and were involved in manuscript writing. Both authors read and approved the final manuscript.

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Availability of data and materials

All data generated or analyzed during this study are included in this published article and its additional information file.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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