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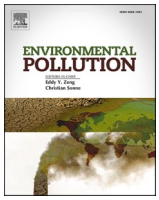

Long-term trends and patterns of legacy and emerging cosmetic UV filters in German waters

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ABSTRACT

Organic UV filters contained in sunscreens and other cosmetics can potentially end up in the aquatic environment. Various studies have demonstrated that UV filters are widespread in water bodies, yet there is a lack of comprehensive understanding of their spatial and temporal distribution in Germany. The objective of this study is to investigate the occurrence of this group of substances in suspended particulate matter (SPM) and water samples, and to explore potential links to market changes reported in the literature. We developed an analytical target method in which SPM was extracted using accelerated solvent extraction (ASE), the extracts were purified, and then analyzed using liquid chromatography-tandem mass spectrometry (LC-MS/MS) with a quadrupole time-of-flight (Q-TOF) mass analyzer. The method detected 10 of 12 organic UV filters in SPM samples from the German Environmental Specimen Bank (ESB). Avobenzone (BMDBM) and iscotrizinol (DBT) showed average concentrations of 105 ng/g dry weight (dw) and 34 ng/g dw, respectively, in 2022. DBT showed a comprehensive significant upward trend at all Rhine stations monitored between 2005 and 2022. Diethylaminohydroxybenzoylhexyl benzoate (DHHB) also showed a clear and statistically significant upward trend at these stations, with a notable increase since 2017 at the Koblenz station. High-resolution mass spectrometry (HRMS) non-target screening (NTS) data confirmed the presence of additional polar organic UV filters in SPM and water samples, specifically camphor benzalkonium methosulfate (CBM), 4-aminobenzoic acid (PABA), ensulizole (PBSA), and sulisobenzone (BP-4). We recommend using a combination of target and NTS methods to achieve a comprehensive assessment of water pollution.

1. Introduction

Organic UV filters are widely used, especially in personal care products (PCPs) and plastics. Many substances act as both UV filters and UV absorbers (Apel et al., 2018), which serve a similar function in providing protection against UV radiation by absorbing it. UV absorbers "protect the cosmetic product from the effects of UV-light" according to the European Commission (European Commission, 2025a). Most UV filters are also UV absorbers, but two UV filters are only listed in Annex VI of the EU Cosmetics Regulation (Regulation (EC) 1223/2009) and are therefore authorized solely for use in cosmetic products with specified concentrations and conditions. These are biscotrizol (MBBT) and phenylene bis-diphenyltriazine (S86) (European Commission, 2025a). Substance regulation is an ongoing, adaptive process. Currently, the EU Cosmetics Regulation lists 29 substances (excluding salts) authorized as UV filters in cosmetic products (European Commission, 2025b). Among these, two are inorganic (ZnO and TiO_2).

Over the last 50 years, the regulation of UV filters in the EU has evolved considerably. UV filters were first included in the Cosmetics Directive in 1976 to address safety, efficacy, and labeling (Council of the European Communities, 1976; Vieira et al., 2024). In 2009, the Directive was replaced by the Cosmetics Regulation (EC) No 1223/2009, harmonizing EU and national legislation. Annex VI of the Regulation lists authorized UV filters following evaluation by the Scientific Committee on Consumer Safety (SCCS), whereas Annex II covers prohibited substances. At its adoption, 27 UV filters were authorized; since then, five new compounds have been added, while 4-aminobenzoic acid (PABA), 3-benzylidenebornan-2-one (3-BC), and 4-methylbenzylidene

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camphor (4-MBC) were banned in 2013, 2015, and 2025, respectively. The new compounds introduced in the list are tris-biphenyl triazine (TBT), added in 2014; ZnO, added in 2016; S86, added in 2019; methoxypropylamino cyclohexenylidene ethoxyethylcyanoacetate (S87), added in 2020; and bis-piperazine (HAA299), added in 2022. It is important to note that the EU Cosmetics Regulation, like the previous directive, assesses the safety of substances for human health but does not provide an environmental risk or hazard assessment. Instead, environmental evaluation falls under the REACH Regulation and requires fate and effect testing based on standardized test guidelines (Pawlowski et al., 2021).

Various studies have shown that organic UV filters are ubiquitous in water bodies (Apel, 2019; Carstensen et al., 2022; Committee on Environmental Impact of Currently Marketed Sunscreens and Potential Human Impacts of Changes in Sunscreen Usage et al., 2022; Fagervold et al., 2019; Mitchelmore et al., 2021; Nagorka and Duffek, 2021). UV filters in sunscreens and cosmetics can enter the environment via various pathways. They can directly enter the environment after being applied to the skin during leisure activities. It is estimated that approximately 25% of sunscreen is washed off during a single recreational swimming event (Danovaro et al., 2008). Alternatively, they can indirectly enter the environment through the wastewater of municipal sewage treatment plants (MSTPs) (Committee on Environmental Impact of Currently Marketed Sunscreens and Potential Human Impacts of Changes in Sunscreen Usage et al., 2022). For wastewater treatment, a distinction can be made between organic UV filters that are readily biodegradable, such as PABA, octinoxate (EHMC), octisalate (EHS), and padimate O (OD-PABA), biodegradable (homosalate (HS), oxybenzone (BP-3), and sulisobenzone (BP-4)), and non-biodegradable (avobenzone (BMDBM), dioxybenzone (BP-8), ecamsule (TDSA), and octocrylene (OC)) (Committee on Environmental Impact of Currently Marketed Sunscreens and Potential Human Impacts of Changes in Sunscreen Usage et al., 2022). A recent study confirmed these findings and added HS as inherently biodegradable, while other organic filters such as bemotrizinol (BEMT), diethylaminohydroxybenzoylhexyl benzoate (DHHB), iscotrizinol (DBT), ethylhexyl triazone (EHT), MBBT, ensulizole (PBSA), S86, S87, and TBT were classified as poorly biodegradable. Using SimpleTreat 4.0, total elimination rates of organic UV filters from water, ranging from 78% to 98% for BP-3, BP-4, BEMT, BMDBM, EHMC, EHS, EHT, HS, MBBT, OC, S86, and TBT, were determined. In contrast, DHHB exhibited a medium elimination rate of 63%, whereas PBSA had a low rate of 25%. Very low elimination rates were calculated for DBT (6%), S87, and TDSA (1% each) (Pawlowski et al., 2025). BP-4 is introduced into the environment through wastewater treatment plant discharges, whereas 4-MBC, amiloxate (IMPC), and OD-PABA are introduced via recreational activities. BP-3, EHMC, and OC were the dominant UV filters in surface water samples, with correlations suggesting that MSTPs are a significant source (Tsui et al., 2014).

Of the non-polymeric organic UV filters authorized in the European Union, over 50% have a calculated log n-octanol-water partition coefficient (log K_{OW}) (US EPA, 2012) greater than four: BEMT, BMDBM, DBT, DHHB, drometrizole trisiloxane, MBBT, HS, EHS, OD-PABA, TBT, EHMC, S86, OC, and EHT. This suggests a tendency to bioaccumulate in organisms or adsorb onto suspended particulate matter (SPM) and sediments (Stec and Astel, 2023). Therefore, these filters should be screened across different matrices. In water PBSA (Neuwald et al., 2021; Scheurer et al., 2023), BP-4 (Carstensen et al., 2022), BP-3, 4-MBC, EHMC (Šauer et al., 2023), OC, HS, EHS, and OD-PABA (Cadena-Aizaga et al., 2020) were previously detected. In sediments, abundant UV filters are BP-3 (Carstensen et al., 2022), HS, OC, EHS, EHMC, BMDBM, and 4-MBC (Cadena-Aizaga et al., 2020; Mitchelmore et al., 2021; Vila et al., 2018). There is also evidence that EHT can be found in sediments (Apel, 2019). Additionally, seasonal variations in concentrations have been observed in sediments in a French lake for DBT and BEMT (Fagervold et al., 2019). In SPM samples from German rivers, EHMC was previously monitored and showed a decreasing average concentration from 18 to 2.9 ng/g dry weight (dw) (Nagorka and Duffek, 2021). A comprehensive overview of the analytical methods used to quantify organic UV filters was published by Cadena-Aizaga et al. (2020).

The scientific literature mentions certain substances, such as 3-BC and 4-MBC, which have been identified as endocrine-disrupting compounds and are associated with specific hazardous properties for humans (Schlumpf et al., 2004; Wang et al., 2016). BMDBM, BP-3, and OC were detected in blood plasma after application (Matta et al., 2020). Studies have shown differences in the hormonal balance of women and men after sunscreen application. BP-3 has been identified as a potential endocrine disruptor with effects on pubertal development in young females (Huang et al., 2021).

UV filters are also known to exhibit ecotoxicological effects in the environment, with potential impacts on corals, algae (OC, OD-PABA (Giraldo et al., 2017), BP-3 (Mao et al., 2017), HS, EHS, and DHHB (Thorel et al., 2020)), arthropods, and fish (3-BC (Kunz and Fent, 2009), BP-3 (Balázs et al., 2016), EHMC (Christen et al., 2011), and OC (Zhang et al., 2016)). Regarding corals, substances such as BP-3, EHMC, and 4-MBC should be specifically mentioned. These substances cause bleaching and negatively affect photosynthetic mechanisms (Chatzigianni et al., 2022; Danovaro et al., 2008). Arthropods, such as *Tigriopus japonicus*, exhibit effects after exposure to 4-MBC (Chen et al., 2018). The larval growth of *Chironomus riparius* was also lower after exposure to this compound. Similar effects were also observed for OC and BP-3 (Campos et al., 2017). *Daphnia magna* is also affected by BMDBM, OC, 4-MBC, EHMC, and BP-3 (Chatzigianni et al., 2022). OC and PBSA exhibited sublethal toxic effects on the mussel *Mytilus edulis*. Additionally, OC accumulates in mussel tissues (Falfushynska et al., 2021). Current research on ecotoxicological effects has focused on specific UV filters, such as BP-3 and 4-MBC (Carve et al., 2021; Hodge et al., 2025). This highlights knowledge gaps, especially for currently used UV filters, such as DHHB, MBBT, and PBSA. Additionally, there is a lack of data concerning the occurrence of UV filters in sediments and their chronic effects on sediment-dwelling organisms (Kroll et al., 2025).

This study investigates the occurrence of UV filters regulated under Annex VI of the EU Cosmetics Regulation in an aquatic environment, focusing on their spatial and temporal distribution. Furthermore, it evaluates whether recent regulatory actions are reflected in environmental concentrations and assesses the associated environmental risks of individual substances.

2. Material and methods

2.1. Selection of relevant UV filters and matrices for monitoring

We initially reviewed the literature as well as the EU Cosmetics Regulation to gain an overview of the full range of potentially environmentally relevant UV filters. Sediments were identified as the preferred matrix for substances with log $K_{OW} > 3$. If the log K_{OW} value was <3, we targeted the investigation in water samples. For compounds with a log K_{OW} between 3 and 5, both matrices were investigated (Ademollo et al., 2012; Loos et al., 2024). Water samples were only investigated using high-resolution mass spectrometry (HRMS) non-target screening (NTS) data.

2.2. Chemicals

The basic information on the UV filters included in this study (CAS No., chemical names, chemical identifiers, suppliers, and purities) is presented in Table S1 in the Supplementary Information. Further information on these substances is provided in Table S7.

Acetonitrile (ACN, LC-MS LiChrosolv), dichloromethane (GC-MS SupraSolv), and formic acid (LC-MS LiChropur) were supplied by Merck (Germany). Water (Chromasolv LC-MS) and sea sand (purified by acid + calcined) were purchased from Honeywell (Germany) and Chemsolute

(Germany). N-hexane (Picograde) and acetone (Picograde) were purchased from scienTEST-bioKEMIX GmbH (Germany).

2.3. Sampling

2.3.1. SPM sampling

SPM samples were provided by the German Environmental Specimen Bank (ESB), a long-term program for sampling, analyzing, and archiving samples from the environment (Conrad et al., 2016). All samples were stored in the ESB above liquid nitrogen at ultralow temperatures (<−130 °C), below the glass transition temperature of water. SPM sampling and processing were performed according to the protocols of the German ESB, as described in previous publications (Keller et al., 2017; Ricking et al., 2012; Wernicke et al., 2022).

The samples were collected monthly using sedimentation traps that accumulate SPM continuously over a one-month period at 13 sites along 7 major German rivers. Monthly samples were stored individually and, at the end of each year, pooled in equal proportions and homogenized, resulting in 13 annual composite samples. The sampling period spans from 2005 to 2022. The selected rivers are part of the 25 largest catchments in Germany, covering different ecosystem types and discharge rates. For instance, the river Saar has an average discharge of 75 m^3/s and a catchment area of 7431 km^2 (Wasserstraßen- und Schifffahrtsverwaltung des Bundes, 2023a). In contrast, the Rhine has an average discharge of 2900 m^3/s and a catchment area of 185300 km^2 (Wasserstraßen- und Schifffahrtsverwaltung des Bundes, 2023b). The concrete information on sampling stations with discharge rates is visible in Table S6 in the Supplementary Information. Further specific information on the sampling sites is described by Fliedner et al. (2016) and Göckener et al. (2022).

For temporal trend analysis, archived ESB samples from three locations at the river Rhine were analyzed from 2005 to 2022 (Weil am Rhein, R1, river km 174; Koblenz, R3, river km 590.3; Bimmen, R4, river km 865). ESB samples from the remaining 10 sites were analyzed for spatial analysis in 2022 (Fig. 1). Due to optimization in the sampling strategy, the German ESB canceled sampling for E3 (Barby, Elbe), D2 (Kehlheim, Danube), and R2 (Iffezheim, Rhine) in 2015. Consequently, these stations were not further considered in this study.

2.3.2. Water sampling

Daily composite water samples were collected from the river Rhine at Koblenz (R3). These samples were collected by the Federal Institute of Hydrology (BfG) at the monitoring station of the International Commission for the Protection of the Rhine (ICPR) using an automated sampling device. Samples were collected as 24-h time-proportional composite samples and continuously stored at 4-6 °C. The sampling procedure has been described previously (Schlüsener et al., 2015). The resulting composite samples represent an integrated average over the 24-h sampling period. The 24-h sample is then mixed to ensure homogeneity and representativeness. For analysis, a 10 mL aliquot was taken from the composite sample. The steel syringe was rinsed three times with MeOH and water, and the first sample draw was discarded. The sample was then filtered through a 0.45 µm syringe filter (CHROMAFIL CA syringe filter, pore size: 0.45 µm). Here, the first milliliter was also discarded. The remaining volume was collected in a 12 mL amber glass bottle. The filtrate is stored at 3-4 °C until processing, and retention samples were stored at −20 °C. For each sampling event, a method blank was generated by filtering and treating ultrapure water in the same way.

2.4. SPM sample extraction for target analysis

The freeze-dried SPM samples were extracted using accelerated solvent extraction (ASE, DIONEX ASE-350). For this purpose, 22 mL stainless steel cells were filled with 3 g of acid-cleaned, annealed (at 450 °C) sea sand, to which 1 g of SPM was added. The SPM was spiked with the isotopically labelled standards BP-3-d_5, OC-[^{13}C]$_3$, 4-MBC-d_4, drometrizole-d_3 (UV-P-d_3), DBT-d_4, and BMDBM-[^{13}C]-d_3. After an equilibration time of 30 min, the cell was filled with 18 g of identical pre-cleaned sea sand. The target levels of the internal standards were in the range of 25 ng/g dw. Extraction was performed using n-hexane/acetone (2:1, v:v) with three 10 min cycles at 100 °C and 100 bar. The ASE extract (≈60 mL) was gently concentrated to dryness under a stream of nitrogen in a water bath (50 °C, TurboVap II, Biotage), reconstituted with 1 mL n-hexane/acetone (0.5 mL 70:30, v:v; 0.5 mL 40:60, v:v), and then purified by solid-phase extraction (Supelclean PSA-SPE tube, PSA weight: 500 mg, volume: 6 mL, Merck, Germany). Two steps of elution were performed using n-hexane/acetone (10 mL at 80:20 and 70:30 v/v). This was followed by concentration to dryness using the same parameters as above. The dried residue was reconstituted in ACN in three 0.25 mL portions and diluted to a final volume of 1 mL with ACN. It was then filtered through 0.2 µm into an amber glass vial with a syringe filter (Omnifix F Solo: Volume: 1 mL, without needle, 3-part, B. Braun SE, Germany; combined with a Sartorius Minisart RC syringe filter: RC, pore size: 0.2 µm, diameter: 4 mm, non-sterile, Sartorius AG, Germany). Each batch of 18 cells included one blank and one duplicate.

2.5. Target analysis of SPM samples from German waters

Instrumental analysis was performed using a UHPLC-MS/MS system (1290 Infinity II coupled to 6545 LC/Q-TOF; both from Agilent Technologies Deutschland GmbH, Germany) equipped with an electrospray ionization (ESI) source and a C18 column (ZORBAX RR Eclipse XDB-C18: HPLC column, dimensions: 80 Å, 2.1 × 150 mm, 3.5 µm, Agilent Technologies Deutschland GmbH, Germany). The mobile phase consisted of A) water with 0.1% (v:v) formic acid and B) ACN with 0.1% (v:v) formic acid. Separation was performed at a constant flow rate of 0.5 mL/min. The solvent gradient started with an isocratic segment of 2% B (1 min) and was then increased to 20% B within 1 min. Within 14.5 min, the percentage of B increased to 98% and held constant for 6.5 min. Measurements were performed in the positive ESI mode for up to 19 min, after which the system was switched to the negative ionization mode. Additional information is available in Table S2 in the Supplementary Information.

2.6. Retrospective HRMS screening of SPM and water samples from German waters

As the applied target analysis method only includes SPM and only a selection of possible samples from the German ESB, results from HRMS NTS measurements were used to assess the complex mixture of organic UV filters in the environment. The German Environment Agency (UBA) and BfG are establishing a national NTSPortal (Dietrich et al., 2022; Jewell et al., 2025c, 2021a, 2021b, 2020; NTSPortal contributors. Federal Institute of Hydrology (BfG), Koblenz, 2025; Nürenberg et al., 2015).

The NTSPortal contains liquid chromatography (LC)-HRMS NTS data from federal and state authorities based on SPM and water samples collected during water monitoring activities. It functions as both a database and a visualization platform, providing SPM data from the ESB with annual resolution, and starting in 2021, even with monthly resolution. In addition, daily resolved water data from Koblenz have been available since 2017, along with further water data from water bodies in Saxony.

All signals displayed in the NTSPortal were verified using standard substances and normalized to bezafibrate-d_6. Analyzing SPM and water samples through non-target analysis and then screening the results retrospectively by a spectral library (Lessmann et al., 2025b) is called DataBase Assisted Screening (DBAS) (Jewell et al., 2025c); however in this study, the commonly applied term HRMS screening is used. As HRMS screening requires reference standards, the processed HRMS NTS data were annotated at the Schymanski level 1 (Schymanski et al., 2014). Consequently, only the substances listed in Table S1 were

screened, and screening for other substances, such as all possible transformation products (TPs), was not performed. The water samples were directly injected (volume: 100 µL), and the preparation of the SPM samples was previously described in another study (Boulard et al., 2020). A short summary of the HRMS screening method was recently published by Köppe et al. (2025). Hosting the NTSPortal requires the use of several software packages, including ntsportal (Jewell et al., 2025b), ntsworkflow (Jewell et al., 2025a), and csl-tools (Lessmann et al., 2025a), which are publicly available at https://github.com/bafg-bund.

2.7. Statistics

All statistical analyses were performed using Python version 3.10.7 (van Rossum, 2010). The following packages were used: NumPy (Harris et al., 2020), pandas, and SciPy (Virtanen et al., 2020). For the descriptive analysis, the time series for each substance and sampling station was smoothed using non-parametric Locally Weighted Scatterplot Smoothing (LOWESS) regression with a smoothing span of 38.9% of the data points, which effectively means a window size of seven for the 18-year measurement data (Cleveland, 1979). A similar approach has been used in other evaluations of German ESB time series data, utilizing an Excel-based tool (Fliedner et al., 2016; Kotthoff et al., 2020). We adapted this tool (Fryer and Nicholson, 1999; Wellmitz, 2014) for Python. Values below the limit of detection (LOD) were set to zero, and concentrations between the LOD and the limit of quantification (LOQ) were substituted with 0.5 × LOQ to account for analytical uncertainty. This commonly applied substitution approach may introduce bias in trend estimation and affect statistical significance, particularly when the proportion of censored data is high. More robust methods for handling censored environmental data, such as maximum likelihood estimation or survival analysis approaches, have been proposed in the literature but were not applied in this study (Gilbert, 1987; Helsel and Helsel, 2012). Correlations were assessed using the Pearson correlation coefficient.

To assess changes between 2005 and 2022, the mean concentrations for both years were compared, and relative changes were calculated. In addition, linear regression analyses were carried out across the full observation period (2005-2022) in the Rhine to estimate continuous trends over time. For each substance and station, a linear regression was performed. A slope $\neq 0$ ($p < 0.05$) was taken as an indication of a decreasing or increasing trend.

2.8. Quality assurance and quality control for the target analysis

As UV stabilizers may be present in laboratory equipment, the use of plastic materials was minimized. All glassware was cleaned in a laboratory dishwasher and annealed at 400 °C.

For quality assurance, recovery tests (n = 16) were performed at two spike levels (20 ng/g dw and 60 ng/g dw), as well as blank determinations (n = 8), to validate the target method. The quality assurance steps and sample processing were repeated after one year. Sea sand was used as a method blank, and the mean blank values for OC, 3-BC, 4-MBC, and BP-3 were 2-13 ng/g dw, which resulted in quantification limits of 9-48 ng/g dw. The blank values of all other organic UV filters analyzed (S87, BMDBM, DBT, DHHB, IMPC, OD-PABA, and UV-P), were between 0-3 ng/g dw.

Quantification was performed using the internal standard calibration method. Calibration was performed on a solvent basis to obtain the response factors of the target analytes to the amount of the corresponding mass-labelled standard. Substances without matching internal standards were fitted with the best matching standard available. For example, DHHB was corrected with DBT-d_4 and showed recovery rates of 83 ± 16%. The recovery rates of UV-P, 3-BC, 4-MBC, IMPC, BMDBM, OC, and S86 deviated from the desired range of 70-130%; therefore, the levels obtained can only be considered semi-quantitative. In future studies, better-suited internal standards with higher structural similarity and better sample preparation should be found for these substances. To check the calibration, a calibration standard of 40 ng/g was included in each batch. The linear calibration functions showed regression coefficients in the range of 0.97-0.99. The detection and quantification limits were obtained from blanks according to Funk (2005). Detection limits between 0.02 (S87) and 16 ng/g dw (OC) were obtained for quantifiable and semi-quantifiable compounds. Additional information is available in Tables S3 and S4 of the Supplementary Information.

All values shown here have been corrected using the absolute recoveries of the mass-labelled standards. The average absolute recoveries ± standard deviation of the mass-labelled standards in the recovery tests (n = 24) were 41.0 ± 6.7% for BP-3-d_5, 11.2 ± 3.7% for OC-[^{13}C]$_3$, 32.4 ± 11.4% for 4-MBC-d_4, 53.3 ± 15.9% for UV-P-d_3, 36.2 ± 4.1% for DBT-d_4, and 4.8 ± 3.4% for BMDBM-[^{13}C]-d_3. The low and variable absolute recoveries of some internal standards may introduce additional uncertainty into the quantification, particularly for compounds with recoveries below 20%.

2.9. Collection of PNEC values and risk characterization

The predicted no-effect concentration (PNEC) values were obtained from the European Chemicals Agency (ECHA) website. The PNEC (sediment freshwater) was used (European Chemicals Agency, 2025a). If no data were available, the PNEC from the 4th Watch List under the Water Framework Directive was employed (Gomez Cortes et al., 2022).

The risk quotient (RQ) was obtained from the maximum measured environmental concentration (MEC_{max}) in the 2022 SPM samples and the PNEC (sediment freshwater) to assess environmental risk via RQ = MEC_{max}/PNEC. If the obtained values are ≥1, a high environmental risk is identified. Values between 0.1 and 1 indicate a moderate risk to (aquatic) organisms. Values between 0.01 and 0.1 indicate a minimal risk, and risk quotients <0.01 indicate no risk (Li et al., 2022). Only values > LOQ were considered for the calculations.

3. Results and discussion

In this study, we focused on all measurable organic UV filters selected based on their potential for environmental release and their authorization as UV filters in cosmetics within the past 20 years. These include 28 UV filters (excluding salts, polymers, and inorganics) listed in the EU Cosmetics Regulation. Additionally, we selected four other substances for screening: 2,3,4-trihydroxybenzophenone (THB), 2,2′,4,4′-tetrahydroxybenzophenone (BP-2), UV-P, and 5-chloro-2-hydroxybenzophenone (BP-7). To gain insight into the metabolites of BP-3, THB was identified as a potentially important compound (Mao et al., 2022; Mutlu et al., 2017). BP-2 is listed in CosIng as a fragrance, light stabilizer, and UV absorber. However, according to CosIng, both UV-P and BP-7 are used as UV absorbers, whereas THB is not listed (European Commission, 2025a). Standard substances for two UV filters (bisdisulizole disodium (DPDT) and PEG-25 PABA) were not purchased, and a standard for HAA299 was not commercially available.

In order to assess the distribution of organic UV filters in the environment, an analytical target method for the determination of these substances in SPM was developed. The method, based on accelerated solvent extraction (ASE), purification by solid-phase extraction with a polymerically bound ethylenediamine-N-propyl phase (PSA-SPE), and subsequent analysis by LC-MS/MS (injection volume: 20 µL), was validated using matrix-containing samples. The following substances were quantifiable: S87, BP-3, DHHB, OD-PABA, and DBT. For UV-P, 3-BC, 4-MBC, IMPC, BMDBM, OC, and S86 only semi-quantitative results were obtained. For the semi-quantitative analyses, it should be noted that the low and variable recoveries may compromise the reliability of the reported concentrations, the derived temporal and spatial trends, and the calculated risk quotients. For future studies of SPM, the spike levels of OC-[^{13}C]$_3$ and BMDBM-[^{13}C]-d_3 should be increased. This addresses their high environmental levels, and it could reduce the variability of the recovery rates.

For polar organic UV filters, the extraction and purification target-method proved to be unsuitable. A better sample preparation must also be found for OC, since the matrix has a strong influence on the ionization of this substance. Furthermore, the reasons for the high blanks of 3-BC, 4-MBC, and BP-3 should be investigated in future experiments. Despite comparatively high detection and quantification limits relative to other studies for some analytes, five of the 12 target analytes could be reliably quantified in SPM, with the remainder assessed on a semi-quantitative basis. Given the quantitative focus of this study and the limited number of analytes, a triple quadrupole instrument may have been more appropriate, highlighting the current limitations of HRMS for strictly quantitative applications. Of the 32 relevant UV filters, three were not purchased (DPDT, PEG-25 PABA, and HAA299) and six were analytically unreachable (HS, EHS, TBT, BEMT, MBBT, and EHT). In summary, this study provides important information on the general distribution of 22 selected organic UV filters in German federal watercourses. HS and EHS could not be detected using the employed analytical methods, highlighting the need for further research in this area. EHMC was not quantifiable because of the absence of a suitable internal standard substance. The other UV filters mentioned are too non-polar for these methods. The target method covered 12 substances, whereas the HRMS screening method covered 21 substances. Only DBT could be measured exclusively using the target method, while the other substances from the target method were covered by the screening method (see Table S5).

3.1. Environmental concentrations of UV filters in German waters

The developed target method covered BP-3, UV-P, 3-BC, IMPC, 4-MBC, DHHB, BMDBM, OC, OD-PABA, DBT, S86, and S87. The measurable substances had a calculated log $K_{OW} > 3$, with the exception of S87 (1.7). In general, substances with a log $K_{OW} < 3$ are more likely to occur in water.

3.1.1. Spatial variability

UV-P was the most frequently detected UV filter (frequency of appearance (FoA): 100%) above the limit of detection (LOD) in the SPM samples collected in 2022 from 13 different riverine sites (Table 1, Fig. 1). BMDBM, DBT, and DHHB were the second most frequently detected (FoA: 92%). The other detected UV filters were detected in the following order: 4-MBC (85%), OC, and OD-PABA (both 77%), 3-BC (29%), BP-3 (23%), and IMPC (8%).

3-BC, which has been banned in cosmetics since 2015, was still measured above the limit of quantification at one monitoring site (FoA: 38%; E2: Zehren, Elbe). S86 and S87 were not detected above the LOD in any of the samples. BP-3 remained under the LOQ in E1 (Prossen, Elbe) and E4 (Cumlosen, Elbe) and at the other monitoring sites under the LOD. The same applies to IMPC, which remained under the LOQ in D1 (Ulm, Danube) and at the other sites under the LOD.

The river Saar showed the highest levels of organic UV filters compared to all other investigated rivers. This is supported by another study that analyzed EHMC in the same SPM samples collected between 2005 and 2017. Elevated levels were found, especially at site S2 (Rehlingen, Saar). This may be due to the low water volume of the Saar (Wasserstraßen- und Schifffahrtsverwaltung des Bundes, 2023a) and urban influences of Saarbrücken and Saarlouis. This is reflected by the high wastewater content relative to the low-water discharge (MNQ), which is between 20% and 30% at S1 (Güdingen, Saar) and between 30% and 50% at S2 (Rehlingen, Saar) (Drewes et al., 2018). S2 reflects the highest category of the wastewater content at all investigated stations in this study and also showed the highest concentrations in 2022 samples for BMDBM and OC.

DHHB was proportionally noticeable in Koblenz (Fig. 2). The proportion of BMDBM remained almost constant across all rivers and accounted for nearly 50% in the Saar. On average, it represents 30% of the detected organic UV filters. DBT is also particularly striking, as this substance is nearly present at all sites and contributes to overall pollution (mean = 13%). 3-BC showed a high proportion (40%) in Blankenese in 2022. The same applies to 4-MBC, with both filters accounting for 80% of the total burden. BP-3, although always below the LOQ, shows a higher load contribution in the Elbe. OC, like BMDBM, was present at all sites in higher percentages and also represented, on average, approximately 30% of the detected organic UV filters. UV-P concentrations varied among the rivers, following the pattern Elbe > Rhine ≈ Danube ≈ Mulde > Saale > Saar. A similar pattern was observed in the SPM analyses of UV-329, which belongs to the same structural class (Wick et al., 2016).

3.1.2. Trend assessment of SPM samples along the river Rhine

This section presents a trend assessment of selected organic UV filters in SPM from the River Rhine, based on annual samples collected between 2005 and 2022 at three monitoring sites: Weil am Rhein, Koblenz, and Bimmen. The long-term dataset allows for a comprehensive evaluation of temporal developments and spatial variability along the river continuum (Fig. 3).

Among the analyzed compounds, DBT and DHHB were particularly prominent in terms of temporal trends. DBT exhibited a statistically significant linear increase at all three sites ($p < 0.001$), with consistent annual slopes of approximately 1.5 to 1.7 ng/g dw, indicating a stable and ongoing input throughout the studied river section. Compared to 2005, the DBT concentrations increased by more than 500% at all sites by 2022.

DHHB has been consistently detected above the LOQ at all Rhine locations since 2008. At the upstream site, Weil am Rhein, the

Table 1
Concentrations (ng/g dw) of UV filters in the annual SPM samples from German waters (2022) with the limit of detection (LOD) and limit of quantification (LOQ). The frequency of appearance (FoA) was calculated using values > LOD. The analyses were performed in duplicate.

				Danube		Elbe				Mulde	Saale	Rhine			Saar	
Analyte	**LOD**	**LOQ**	**FoA (%)**	**D1**	**D3**	**E1**	**E2**	**E4**	**E5**	**Mu**	**Sa**	**R1**	**R3**	**R4**	**S1**	**S2**
UV-P	1.6	4.6	100	<LOQ	<LOQ	7	12	5	6	5	8	7	10	15	6	13
BMDBM	4.4	13	92	84	32	77	89	15	<LOD	42	86	86	59	48	219	527
DBT	1.1	3.4	92	45	9	37	32	14	<LOD	14	50	48	29	23	73	67
DHHB	0.04	0.12	92	10	1	11	6	1	<LOD	2	10	13	58	16	49	42
4-MBC	3	9.1	85	19	<LOQ	<LOQ	66	14	15	<LOD	25	<LOQ	<LOQ	<LOQ	<LOD	<LOQ
OC	16	48	77	160	<LOD	146	62	<LOQ	<LOD	<LOD	114	97	102	84	133	292
OD-PABA	0.04	0.11	77	<LOQ	<LOD	0.12	<LOQ	<LOQ	<LOD	<LOQ	0.19	<LOD	<LOQ	<LOQ	0.26	0.23
3-BC	9.6	29	38	<LOQ	<LOD	<LOQ	32	<LOD	<LOQ	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BP-3	7.8	23	15	<LOD	<LOD	<LOQ	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
IMPC	1.1	3.2	8	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
S87	0.02	0.05	0	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
S86	0.02	0.05	0	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sum of organic UV filters				318	42	278	299	49	21	63	293	251	258	186	480	941

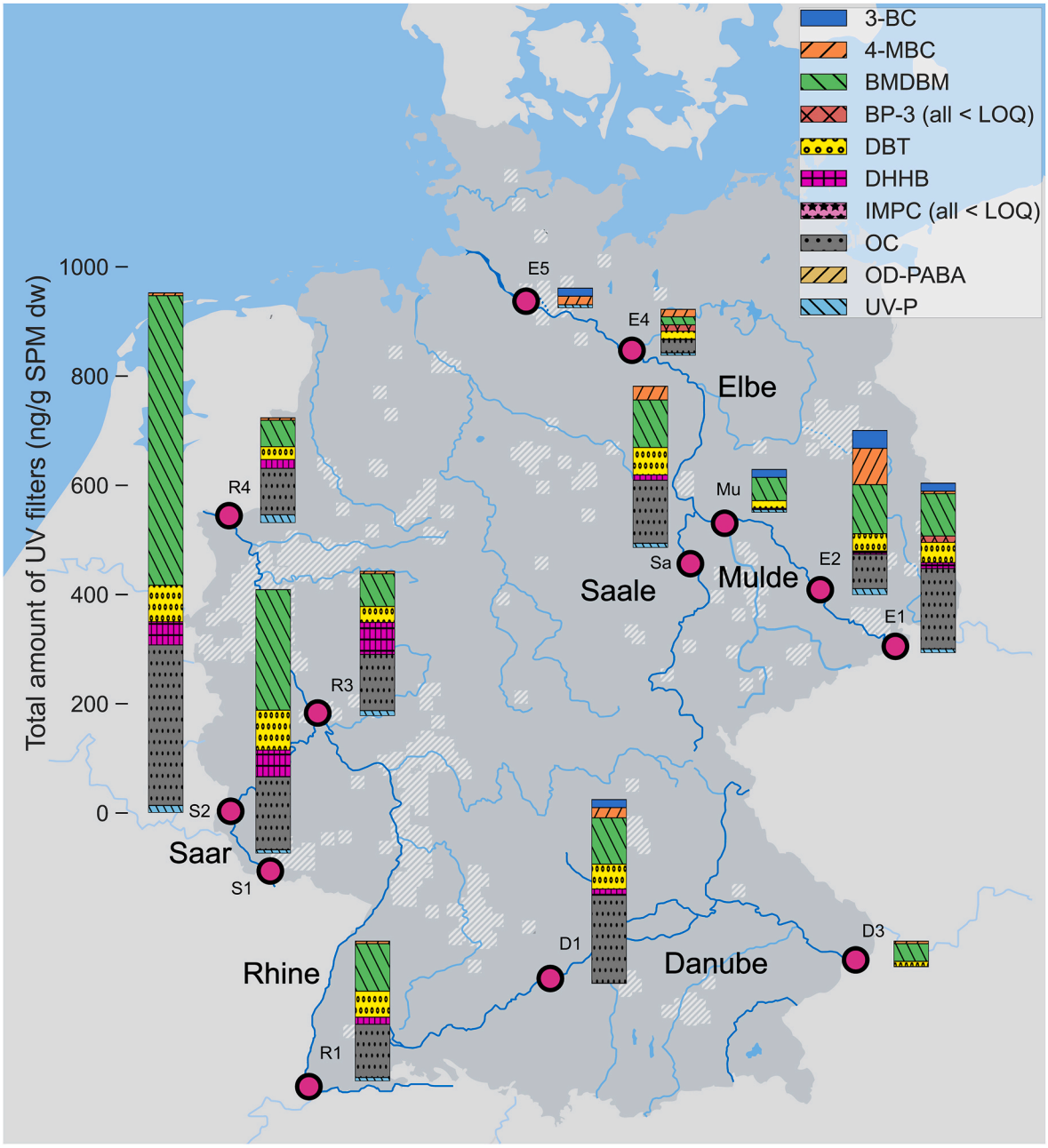

Fig. 1. Total amounts of organic UV filters measured at the sampling sites of the SPM in 2022. The S86 and S87 values were always < LOD. Values below the limit of detection (LOD) were set to 0 ng/g, and those between the LOD and the limit of quantification (LOQ) were set to 0.5 × LOQ (Source: UBA).

concentrations peaked markedly in 2016 before declining. In contrast, downstream locations (Koblenz and Bimmen) showed a notable increase in DHHB levels beginning in 2017. This may indicate an association with industrial production or discharge activities in the middle section of the Rhine (upstream of Koblenz), where UV filter production activities have been reported (Kuntz, 2019; Satyanarayan and Wesche, 2020; Umweltbundesamt, 2025). A similar influence of industrial sources has been proposed to explain the elevated EHMC levels at Koblenz (Nagorka and Duffek, 2021). However, a direct source attribution cannot be established based on the available data. Between 2005 and 2022, the DHHB concentrations increased by more than 10000% at all Rhine sites. DHHB showed, similar to DBT, a significantly increasing linear trend ($p < 0.001$) with slopes ranging from 0.7 to 2.2 ng/g dw increase per year.

BMDBM demonstrated a statistically significant linear increase at Koblenz ($p < 0.03$), with a slope of 1.4 ng/g dw per year. Compared to 2005, at Bimmen, concentrations decreased by 33% to 2022, while at Koblenz and Weil am Rhein, at the same time period, increases of 799% and 29%, respectively, were observed. OC showed over the years in the Rhine a significantly increasing linear trend ($p < 0.01$) only in Koblenz, with a slope of 3.8 ng/g dw per year. At all sites, an increase in concentrations was observed in 2022 compared to 2005, with Weil am Rhein showing only a 10% increase, Bimmen 252%, and Koblenz 326%. IMPC remained below the LOD throughout the study period, and OD-PABA remained below 0.5 ng/g. UV-P showed no discernible temporal trends but a high in 2007 in Bimmen. BP-3 was detected in 2015 and 2016 at Weil am Rhein. In the preceding years, it was occasionally detected in Bimmen and Koblenz. It was last detected in Bimmen in 2018. This pattern could result from the ongoing regulatory evaluation of the compound under REACH (Community Rolling Action Plan (CoRAP)), initiated in 2013 (European Chemicals Agency, 2025b), and

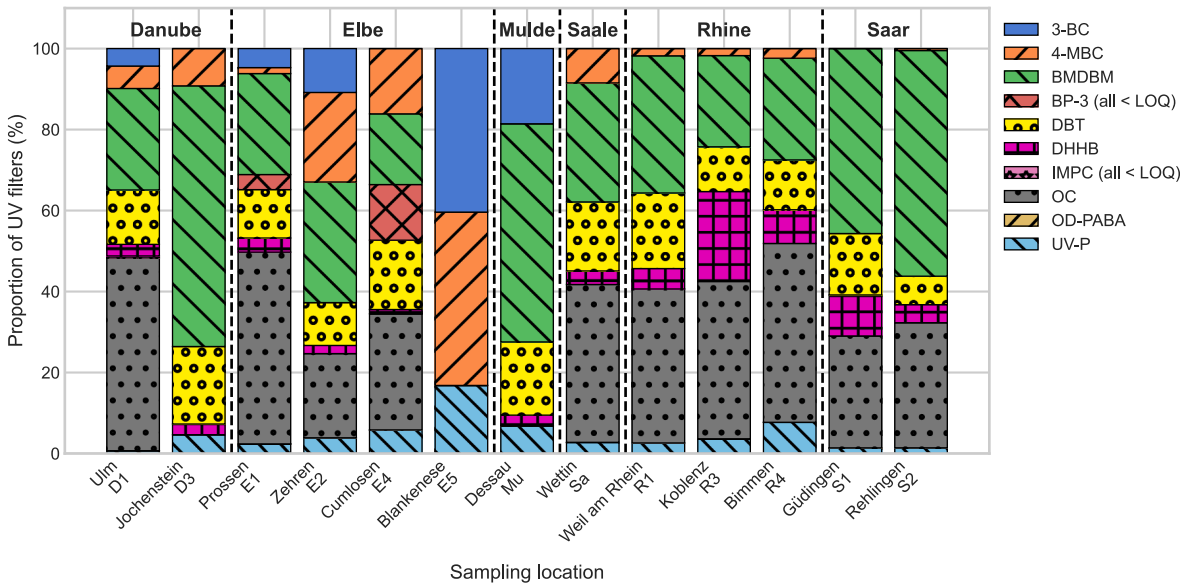

Fig. 2. Relative distribution of organic UV filters at each SPM sampling site, normalized to 100 %.

the ongoing reduction of the allowed content in cosmetics (European Commission, 2022a, 2017). 3-BC has been banned in cosmetic products in the EU since February 2016 (European Commission, 2015a). The compound peaked in 2010 at Bimmen and in 2012 at Koblenz. In 2017, it fell under the LOD in Weil am Rhein. The same occurred in 2020 in Koblenz and in 2022 in Bimmen. By 2022, it was no longer detected above the LOD at any Rhine site, representing a 100% reduction compared to 2005.

A moderate negative correlation was observed between historical EHMC values (Nagorka and Duffek, 2021) and both DBT ($r = -0.43$, $p < 0.05$) and DHHB ($r = -0.42$, $p < 0.05$), suggesting a potential substitution over time. Positive correlations were found between DBT and BMDBM ($r = 0.65$, $p < 0.002$), DHHB and BMDBM ($r = 0.38$, $p < 0.002$), OC and BMDBM ($r = 0.51$, $p < 0.001$), and DHHB and DBT ($r = 0.59$, $p < 0.001$). The normalization of concentrations to the total organic carbon (TOC) content in SPM was investigated. However, this did not affect the trends observed. A moderate correlation with TOC content was observed for DBT ($r = 0.47$, $p < 0.02$) and a weak correlation for DHHB ($r = 0.27$, $p < 0.03$). The trends are shown in Fig. S1 in the Supplementary Information. All results of the target analysis are available in Table S8.

The trends of organic UV filters in German water bodies follow the changes in regulation and the European market (Fig. 4). It should be noted that the actual market time trends potentially differ from the trends shown because only time-specific market studies were used. To the best of our knowledge, real-time market monitoring or historical data are not available in the EU. BP-3 and OC have not been removed from the EU Cosmetics Regulation but have been nevertheless subject to revised concentration limits following safety assessments by the SCCS. These revisions have resulted in stricter conditions of use, particularly for specific product categories. The Scientific Committee on Consumer Products (SCCP) recommended reducing the content of BP-3 in cosmetic products in 2008 (Scientific Committee on Consumer Products (SCCP), 2008). This reduction was implemented in 2017 for all products and again in 2022 for specific products as part of the EU Cosmetics Regulation, due to evidence of endocrine-disrupting effects and high systemic exposure. Additionally, a visible warning label stating "contains benzophenone-3" is required. BP-3 was originally permitted in sunscreens at concentrations of up to 6% (European Commission, 2022a, 2017). OC was added to the CoRAP list in 2012 due to the request for additional information (European Chemicals Agency, 2025c). OC was permitted throughout the EU at concentrations of up to 10%. In 2022, a reduced limit of 9% was introduced for aerosol spray products. In addition, it must be verified whether benzophenone (BP), a degradation product of OC, is present only in trace amounts (European Commission, 2022a). Furthermore, France recently postponed the submission of the Annex XV restriction proposal on OC to 18th July 2025. It has been classified by the French Agency for Food, Environmental and Occupational Health & Safety (ANSES) as harmful to aquatic ecosystems (European Chemicals Agency, 2024). DBT was added to the CoRAP list in 2015, and the assessment concluded by the ECHA found that DBT is highly persistent and does not meet the PBT or vPvB criteria (European Chemicals Agency, 2025c, 2023). Regarding DHHB, we could not find any specific regulatory actions. HS was re-evaluated because of potential hormonal effects. In 2021, the SCCS concluded that HS was not safe at concentrations of up to 10%. As a result, the EU restricted its use in 2022 to a maximum of 7.34%, and only in face products, excluding propellant-driven spray products. This effectively means that HS is no longer permitted in body sunscreens (European Commission, 2025b). EHMC is still permitted at concentrations of up to 10%. Its safety was confirmed by the SCCS in 2025. However, it has been demonstrated that estrogenic activity and weak anti-androgenic activity can be observed both in vitro and in vivo (Scientific Committee on Consumer Safety (SCCS), 2025). Cosmetic products containing 3-BC have not been permitted for sale since February 2016 in the EU. 4-MBC was previously authorized for use at concentrations of up to 4%. However, in 2022, the SCCS was unable to confirm its safety, leading the EU to adopt a ban effective from 1st May 2025 (European Commission, 2025b; Scientific Committee on Consumer Safety (SCCS), 2022). OD-PABA, a derivative of the banned PABA, is still permitted for use in cosmetic products at concentrations of up to 8% (European Commission, 2025b).

Several organic UV filters have been included in the EU Watch List of substances for Union-wide monitoring to generate occurrence data needed for risk assessment. In 2015, EHMC was added to the 1st Watch List and delisted in 2018 (European Commission, 2018, 2015b). In 2022, BP-3, OC, and BMDBM were included and carried over to the 5th Watch List (European Commission, 2025c, 2022b). Most recently, EHS was included in 2025. Although these substances are predominantly adsorbed onto SPM because of their hydrophobic properties, the monitoring requirements of the watch list focus on their analysis in water, potentially underestimating their actual environmental burden (European Commission, 2025c).

These regulatory actions have impacted the European market. The prominent UV filters in 2005 were 4-MBC, BP-3, EHMC, and TDSA. In

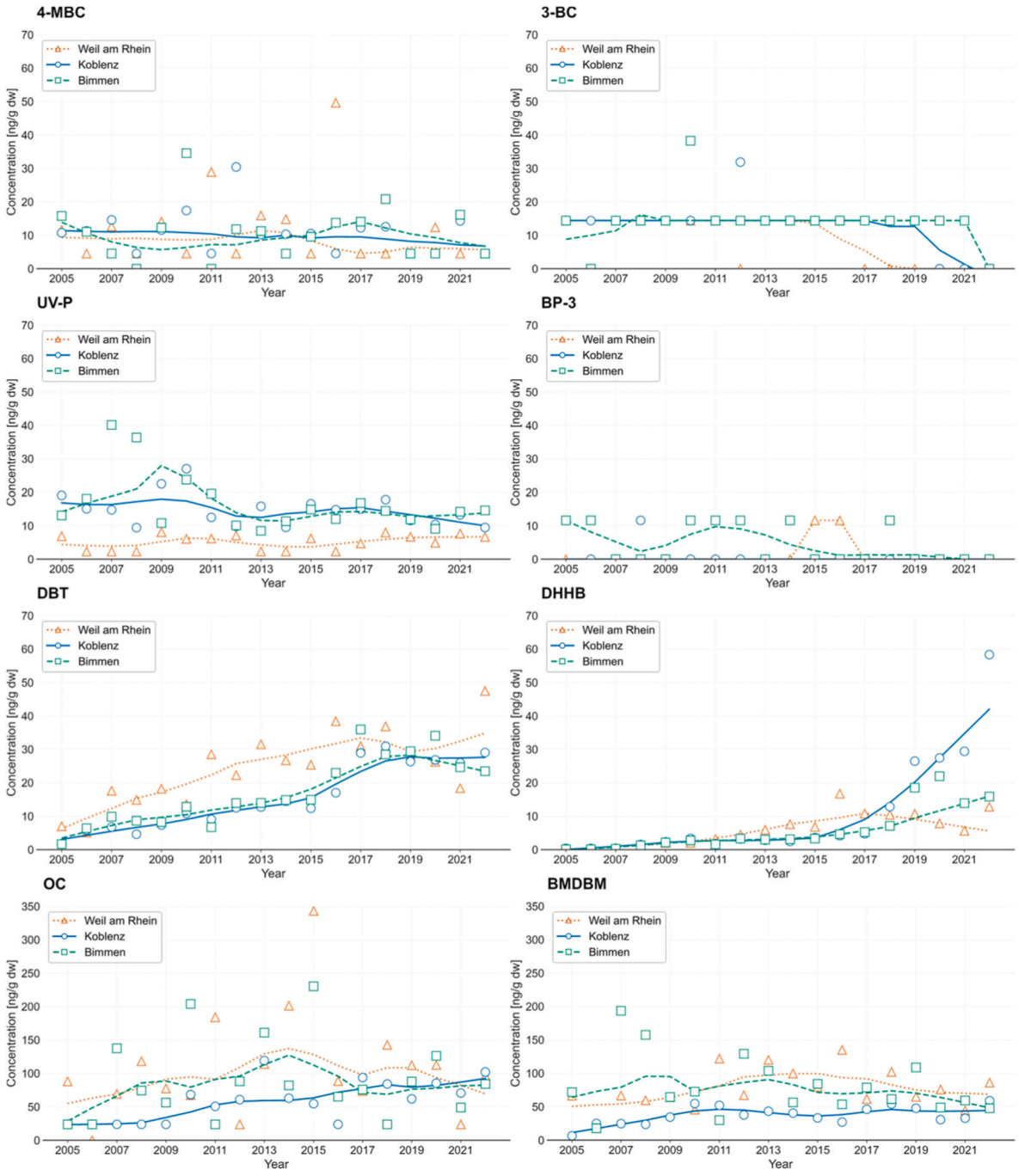

Fig. 3. Time trends of the concentrations of organic UV filters in SPM (dry weight, dw) in ng/g. Displayed are LOWESS-smoothed trends (smoothing span: 38.9% of data points) and individual measurements from the Koblenz, Bimmen, and Weil am Rhein stations (2005-2022). Values below the limit of detection (LOD) were set to 0 ng/g, and those between the LOD and the limit of quantification (LOQ) were set to 0.5 × LOQ. The scale on the y-axis for OC and BMDBM (both semi-quantitative) is different because of the high concentrations found.

2023, the usage of these UV filters changed in Europe. The use of several UV filters has increased over the years (for example, BEMT, DBT, HS, IMPC, and OC), with a particularly high increase in the use of DHHB (10x), HS (6x), MBBT (3x), and PBSA (3x). The use of 4-MBC and EHMC has decreased over the years by −96% and −56% (Jesus et al., 2022; Kerr, 2011; Pniewska and Kalinowska-Lis, 2024; Wahie et al., 2007). These changes are evident in the environment, and we can confirm that the levels of 3-BC, EHMC, and BP-3 have decreased. The period of dominance of OC and BMDBM around 2010 has also passed, and other filters have emerged, such as the very persistent DBT and, especially, DHHB. This aligns with various German human biomonitoring (HBM) studies that have demonstrated a significant increase in DHHB since 2012. Notably, 4-MBC was detected in half of the HBM samples in 2005, but its presence was no longer observed in 2019. In contrast, OC has shown a substantial increase since 2000 and reached its peak in 2016 in human urine samples (Bury et al., 2023; Murawski et al., 2021; Scherer et al., 2025; Schmidtkunz et al., 2023). Regulatory actions appear to be catalysts for this change. This implies that the products used on the market have an impact on humans and ultimately the environment.

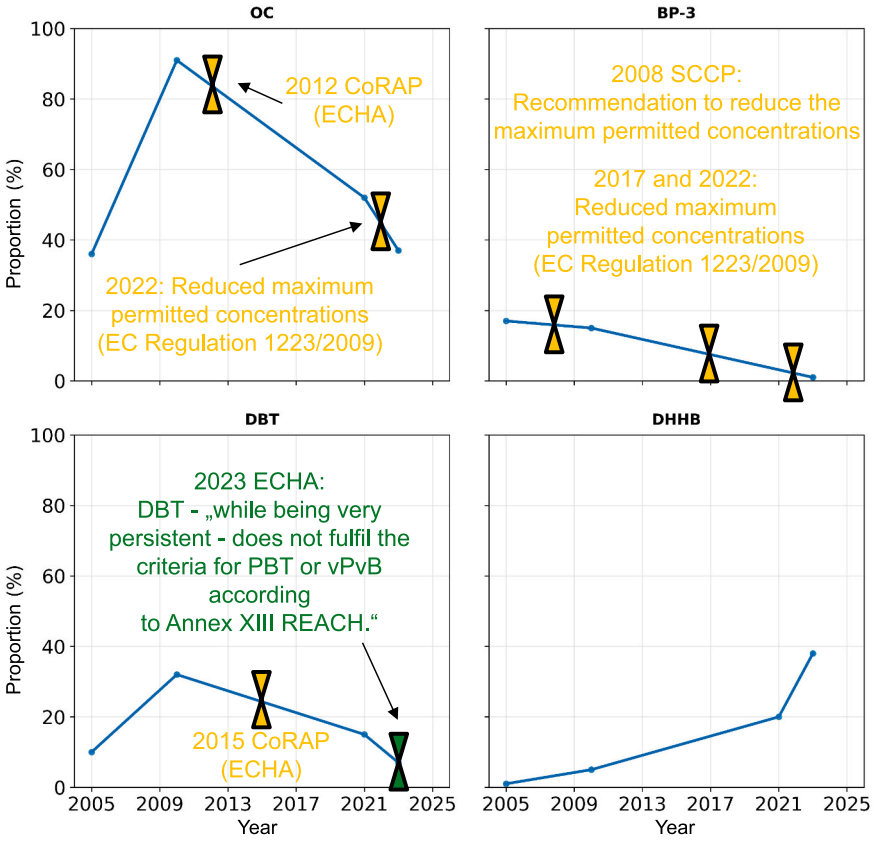

Fig. 4. Proportion of sun protection products containing specific UV filters (examples compiled from Jesus et al., 2022; Kerr, 2011; Pniewska and Kalinowska-Lis, 2024; Wahie et al., 2007) linked with specific regulatory actions (European Chemicals Agency, 2025c, 2024, 2023; European Commission, 2022a, 2017; Scientific Committee on Consumer Products (SCCP), 2008). Reductions in the maximum permitted concentrations in cosmetics or CoRAP listings are indicated by orange sandglasses, while green ones indicate all-clear reports. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.2. Retrospective HRMS screening of SPM and water samples from German rivers

Using the HRMS screening approach, four additional organic UV filters were detected beyond those identified in the targeted analysis. These include camphor benzalkonium methosulfate (CBM), which has not been reported in the environment to the best of our knowledge, PABA, and PBSA in SPM. In Koblenz water samples, these compounds were PBSA and BP-4.

In SPM, PABA was detected at 11 out of 13 sites in all years, with decreasing trends ($p < 0.05$) in R4, E5, and S2, a rising trend in E2, and no trends at the other sites. PBSA was detected in 7 of the 13 stations and showed rising trends in E4, Mu, and R3 with a decreasing trend in S1 and no trends at the other stations. CBM was detected at 12 out of 13 stations, with no detection at R1. It mostly showed decreasing trends, except for an increasing trend in Mu. No trends were visible at the Elbe, except at E5. For the other substances, the trend assessment using targeted and non-targeted approaches did not differ. For example, DHHB

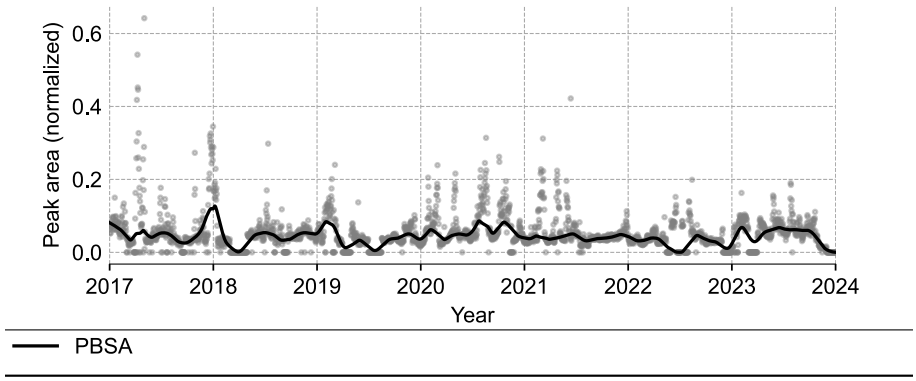

Fig. 5. NTSPortal time trend of the normalized peak area of PBSA (ESI positive) in water (normalized to bezafibrate-d_6). Displayed are LOWESS-smoothed trends (smoothing span: 3% of data points) and individual measurements from the Koblenz station (2017–2024).

was detected at 11 out of 13 stations and also showed rising trends in the Rhine stations, as verified by the targeted analysis (R1, R3, and R4), as well as at the Saar (S1 and S2), Elbe (E1 and E2), Saale (Sa), and Danube (D1) stations. This demonstrates the widespread use of this substance and the benefits of an effective NTSPortal monitoring approach. The highest peak area and concentration were measured in Koblenz (R3) in 2022, which supports the target results. 4-MBC was detected at seven of the 13 stations and showed a rising trend only in Mu. OC was detected at 10 of the 13 stations. BMDBM was detected at every station and in every year. Further studies should test the possibility of verifying the NTSPortal results through a semi-quantification approach.

In the water samples from Koblenz (R3), OD-PABA, UV-P, PBSA (Fig. 5), DHHB, BP-4, OC, BMDBM, and IMPC were detected. OD-PABA, PBSA, DHHB, BP-4, and OC exhibited a significant decreasing trend ($p < 0.05$), whereas BMDBM showed a significant increasing trend ($p < 0.05$). All HRMS screening results are available in Table S9. The NTSPortal time trend of PBSA (ESI positive) in water shows frequent detection (85% from 2017 to 2024) of the substance, with noticeable peaks in the trend. The highest measured normalized peak area (0.642) was 12 times higher than the mean normalized peak area (0.052) during this period.

We conclude that this group of substances should be screened in different environmental matrices, such as water and SPM. The overlap between the target study and the results from the NTSPortal was quite high, particularly in the samples collected in Koblenz in 2022 and the trend analysis conducted on Rhine samples. Most of the results are consistent, but for OD-PABA, which was detected in very low concentrations in 2022 in SPM samples, the concentrations were potentially too low to be detected using the HRMS screening method. UV-P is often detected using the target method, but only in Rehlingen (S2, Saar) in the NTSPortal, which could be potentially due to blank corrections. Overall, the HRMS screening results could be useful for prioritizing substances that require a targeted method of analysis. As only the HRMS screening approach was used, there is potential for further suspect screening to identify relevant TPs. This is a potentially intriguing topic for future research because there is a possibility that the toxicity of the TPs could be higher than that of the native substance (Carstensen et al., 2022).

3.3. Risk characterization

When interpreting the evaluation, it is crucial to acknowledge that a comprehensive risk assessment is not yet entirely feasible. An example is 4-MBC, which poses a potential risk to sediment-dwelling organisms. However, there is currently no PNEC (sediment) value available for this compound because there is no active REACH registration dossier (Table 2), which is also the case for 3-BC. Therefore, risk calculation was not possible.

Table 2
Risk assessment of the occurrence of organic UV filters in SPM.

Substance	PNEC (Sediment, µg/kg dw, (European Chemicals Agency, 2025a))	MEC_{max}/ PNEC (2022)	Linear trend in the Rhine (2005-2022, $p < 0.05$)
3-BC	-	-	decreasing trend in Koblenz
4-MBC	-	-	no trend
BMDBM	11960 [a]	0.04	rising trend in Koblenz
BP-3	66	MEC < LOQ	no trend
DBT	17500	<0.01	rising trend at all three sites
DHHB	536	0.11	rising trend at all three sites
IMPC	90.6	MEC < LOQ	-
OC	1302000	<0.01	rising trend in Koblenz
OD-PABA	42.1	<0.01	decreasing trend in Koblenz
S87	40.5	MEC < LOD	-
S86	-	MEC < LOD	-
UV-P	136	0.11	no trend

[a] 4th EU Watch List under the Water Framework Directive (Gomez Cortes et al., 2022).

Risk quotients for DHHB, UV-P, and BMDBM, on the other hand, could be calculated and suggest a moderate level of risk for DHHB and UV-P ($0.1 < RQ < 1$) and a low risk for BMDBM ($0.01 < RQ < 0.1$), even if an extended measurement uncertainty (100%) is applied to the semi-quantitative result of BMDBM. Moreover, the increasing trends observed in the Rhine imply that substances such as BMDBM, DBT, DHHB, and OC may pose a growing risk in the future. However, a realistic risk scenario exists for DHHB, which has shown a significant increase in recent years. Assuming exponential growth in Koblenz (R3), the PNEC could be exceeded by 2028. The precise point source of DHHB remains unknown, necessitating further analysis of water and suspended particulate matter (SPM) samples. In contrast, station R3 (Koblenz, Rhine) exhibits no significant anomalies for the other UV filters. However, DHHB stands out in both target and NTSPortal results at this location, suggesting the possible contribution of additional sources beyond a municipal sewage treatment plant (MSTP). It is crucial to investigate whether future samples reveal similar patterns. The mixture risk calculation of these results is also crucial, but it was not conducted in this study. Future research should specifically address PNEC values, as well as the assessment factors and physicochemical properties used to determine them. Quantifying NTSPortal results could aid in conducting a comprehensive risk assessment of organic UV filters in German water bodies. For PBSA, it was demonstrated that the concentrations in water samples, which correspond to the normalized peak areas, are 12 times higher than the long-term annual mean. Consequently, the risk to aquatic organisms could also be higher.

4. Conclusions

This study shows the widespread occurrence of organic UV filters in German water bodies and the dynamic change in the market using long-term archived SPM samples. In 2022, substances such as BMDBM, DHHB, and DBT were detected in 12 out of 13 monitoring stations of the German ESB at mean concentrations of 105 ng/g dw for BMDBM, 17 ng/g dw for DHHB, and 34 ng/g dw for DBT across all monitoring stations in 2022.

The authors propose including DHHB and DBT in the EU surface water watch list in the future. The data collected in this study indicate an increasing use of DHHB in Germany. This is further supported by the increased detection of a di-n-hexyl phthalate (DnHexP) metabolite in human biomonitoring samples (Scherer et al., 2025), which is likely linked to phthalate impurities in DHHB-containing sunscreen formulations. Consequently, enhanced monitoring of DHHB is recommended in water, SPM, and sediments. The market data from recent studies suggest that the use of DHHB has increased significantly compared to 2005, so nearly four in 10 products contained DHHB in 2023. In contrast, DBT does not appear to be used more frequently than in 2010 (Jesus et al., 2022; Kerr, 2011; Pniewska and Kalinowska-Lis, 2024; Wahie et al., 2007). The primary concerns revolve around the potential effects of DHHB on aquatic organisms, which have not been a focus in previous studies. Additionally, the long-lasting nature of DBT raises concerns about its environmental impact. Notably, these two substances are also nearly ubiquitous in SPM samples.

In addition to the target analysis, HRMS screening (Jewell et al., 2025c), in which SPM samples were analyzed through non-target analysis and then retrospectively screened by a spectral library (Lessmann et al., 2025b), was demonstrated as a complementary method capable of identifying additional UV filters (CBM, PABA, PBSA, and BP-4) not included in the target method. These, mostly water-soluble compounds, should be included in future monitoring studies to determine their environmental impact.

The market significantly changed over the study period from 2005 to 2022, demonstrating that regulatory actions directly impact the market. Through the use of HRMS NTS data, substances can be detected early in monitoring activities after they have been marketed. However, a crucial prerequisite is that monitoring laboratories are legally provided with standard substances by manufacturers to monitor substances in real time. This provides comprehensive protection for both humans and the environment. Another finding of this study is that implementing novel monitoring approaches, such as HRMS screening, substantially increases the volume of monitoring data for a wide range of compounds. Consequently, the new challenge lies in acquiring high-quality ecotoxicology data to accurately calculate PNECs for individual substances and mixtures. This endeavor will help bridge data gaps and pave the way for the development of inherently safe and sustainable substances.

CRediT authorship contribution statement

Eric Winter: Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Jan Koschorreck:** Writing – review & editing, Supervision, Project administration, Conceptualization. **Luise Brendler:** Validation, Methodology, Investigation, Formal analysis, Data curation. **Thomas Backhaus:** Writing – review & editing, Data curation. **Anja Duffek:** Writing – review & editing, Validation, Supervision, Project administration, Data curation, Conceptualization.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and material

All data generated or analyzed during this study are included in this article and Supplementary Information.

Safety

There are no unexpected or significant hazards associated with the reported work.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work the authors used DeepL and ChatGPT in order to improve language and readability. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2026.128343.

Data availability

All data generated or analyzed during this study are included in this article and Supplementary Information.

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