



Baseline

Baseline monitoring of organic sunscreen compounds along South Carolina's coastal marine environment

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ABSTRACT

Organic ultraviolet filters (UV-F) are increasingly being used in personal care products to protect skin and other products from the damaging effects of UV radiation. In this study, marine water was collected monthly for approximately one year from six coastal South Carolina, USA sites and analyzed for the occurrence of seven organic chemicals used as UV filters (avobenzene, dioxybenzone, octocrylene, octinoxate, oxybenzone, padimate-o and sulisobenzene). The results were used to examine the relationship between beach use and the distribution of UV-F compounds along coastal South Carolina, USA. Five of the seven target analytes were detected in seawater along coastal South Carolina during this study. Dioxybenzone and sulisobenzene were not detected. The highest concentrations measured were >3700 ng octocrylene/L and ~2200 ng oxybenzone/L and beach use was greatest at this site; a local beach front park. Patterns in concentrations were assessed based on season and a measure of beach use.

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Organic ultraviolet filters (UV-F) are photo-active chemicals that are used in a number of industries to minimize the effects of light and their use has increased steadily. In addition to serving as active ingredients in sunscreen lotions and sprays, organic UV-F chemicals have been used in other cosmetic products for nearly 75 years (Giokas et al., 2007). They are also often found in plastic food coverings in order to enhance food preservation and processes related to pharmaceutical and agro-chemical production (Díaz-Cruz et al., 2008; Gago-Ferrero et al., 2012). Annual sales of sunscreens alone exceeded \$600 million in the U.S. during the late 1990s (U.S. FDA Department of Health and Human Services, 1999). Organic UV-F chemicals act as an absorbance medium for light energy and are generally hydrophobic, aromatic structured compounds. Many of these chemicals have high octanol water partitioning coefficients (K_{ow}), indicating the compounds preferential association with particulate organic matter in the environment (Rodil and Moeder, 2008). Common UV-F chemicals used in

commercial products include oxybenzone (benzophenone-3), dioxybenzone (benzophenone-8), sulisobenzene (benzophenone-4), avobenzene, octocrylene, octinoxate (ethylhexyl methoxycinnamate; EHMC), and padimate-O.

In a recent review Díaz-Cruz and Barceló (2009) examined hormonal responses under UV-filtering chemical (such as 4-methylbenzylidene camphor, octinoxate and oxybenzone) exposures. These chemicals have been reported to elicit *in vitro* and *in vivo* hormonal activity in MCF-7 cells (Schlumpf et al., 2004) and have been shown to be genotoxic to yeast cells (Negreira et al., 2009). The induction of vitellogenin between 600–750 µg/L (Fent et al., 2010) and feminization in sex characteristics of male fish at ~1 mg/L has also been associated with frequently used UV filters (Díaz-Cruz and Barceló, 2009). In addition, these compounds have been reported to act as endocrine disruptors in fish at levels <1 µg/L and cause acute toxicity in *Daphnia magna* at concentrations up to ~50 mg/L depending on the chemical (Fent et al., 2010; Brausch and Rand, 2011), as well as induce bleaching in corals (Danovaro et al., 2008). Increased controversy regarding consumer safety and the potential for environmental impacts of organic UV-F chemicals over the past decade has led to an increased concern over the usage of the compounds in commercial products and their presence in the environment.

Despite the growing knowledge about the toxicological effects of UV filtering compounds on aquatic organisms, reports on the occurrence of sunscreen chemicals in natural waters have been limited and generally

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focused on swimming/bathing waters in closed systems (*i.e.*, swimming pools or small lakes) (Díaz-Cruz et al., 2008). Direct release of UV filtering chemicals into the aquatic environment from bathing and swimming activities is reported as a major environmental source of these chemicals (Giokas et al., 2007). It is likely then that release to the environment may occur in beachfront and near-shore ecosystems, as these areas often support extensive recreational beach use where sunscreen use is encouraged.

The objectives of this study were to determine the occurrence and concentrations of seven organic UV-F compounds in coastal waters of South Carolina (SC), USA, to examine the relationship between chemical concentration and beach use, and to examine temporal patterns. Areas along the coast of SC support different levels of development and tourism based recreation; understanding the trends associated with season and beach use may provide coastal managers with information that can be useful for evaluating the potential hazards associated with UV-F chemicals.

Six sites were selected spanning over a 100-mile range of the coast of SC (Table 1). All of the sites allowed for beach access, however, the accessibility and amenities provided varied. Selected sites ranged in use patterns from limited use areas including a reference station within the North Inlet-Winyah Bay National Estuarine Research Reserve (NERR) (NI; Site 2) to areas that support higher development density and coastal tourism, like the Fishing Pier on Folly Island (FP; Site 5) (Fig. 1). Other sites included in this study are beach stations along the northern SC coast (Myrtle Beach, vacation destination, MB; Site 1), an abandoned U.S. Coast Guard station that has since been protected as an open and undeveloped park (CG; Site 3), a beach location dominated by residential beach front homes (WO; Site 4) and a family centered beachfront park with amenities such as showers, restrooms and a small beach store (CP; Site 6). The park (Site 6) was severely impacted by winter storms during the study period and was closed due to beach erosion during the fall of 2011.

Tides were evaluated so that water samples were collected at low tide and near midday. Water was sampled (September 2010–October 2011) by walking approximately 1.5 m into the ocean at low tide, and collecting 1-liter of sub-surface water in solvent rinsed glass jars. Samples were held in a cooler, transported back to the laboratory and stored at 4 °C until extraction the following day. Each site was visited monthly for approximately one year resulting in sampling sizes of $n = 13$ at Sites 3, 4, 5 and 6; $n = 12$ at Site 1; and $n = 11$ at Site 2 (Fig. 1). As a general assessment of beach use, the number of people found within a 25 m

radius around the collection point at each site at the time of sampling was determined. Count data included people using the water at the time of sampling as well as those that were on the beach. This sampling design allowed for comparisons of UV filter concentrations in marine coastal ecosystems of SC based on seasonal and beach use (count data) patterns.

All samples were extracted and quantified using the method presented in Bratkovics and Sapozhnikova (2011). Briefly, a 200 mL water sample was acidified to pH 2 using hydrochloric acid and extracted using Oasis HLB cartridges (500 mg bed mass, 6 mL solid phase extraction cartridge). The compounds of interest were eluted with 36 mL of a 1:1 mixture of methanol and acetone (by volume). In order to assure data quality, a series of reagent blank samples and matrix spike samples were prepared and analyzed along with monthly samples. Data was determined to be acceptable for each batch of samples when spike recoveries were $100 \pm 20\%$.

Chromatographic separation was achieved using an Agilent 1100 HPLC with a Waters XBridge C18 column (2.5 μm , 2.1 mm x 50 mm). The LC gradient is detailed in Bratkovics and Sapozhnikova (2011) and included a 95%/5% ratio of aqueous formic acid (0.1%)/acetonitrile buffer and 100% acetonitrile. Sample analysis flow rate was 450 $\mu\text{L}/\text{min}$. The LC was coupled with an API 4000 mass spectrometer (Applied Biosystems/MDS Sciex, Ontario, Canada) with electrospray ionization (ESI) as a source for analytical quantification. Analytes were detected in ESI positive mode using multiple reaction monitoring (MRM). Two MRM transitions were used to identify the analytes with transition ratios used for confirmation. The calculated detection limits according to Vanderford et al. (2003) were 12.5 ng/L for dioxybenzone, sulisobenzene, and padimate-O; 1 ng/L for avobenzene; 0.5 ng/L for oxybenzone and 25 ng/L for octocrylene and octinoxate. Concentrations of target analytes measured below the method reporting limit (MRL) of each compound were replaced with zeros for the purposes of data analysis. An alpha level of 0.05 was used for all statistical tests.

A nonparametric multiple comparison (Wilcoxon Each Pair, JMP11) test was completed for each UV-F chemical to identify significant site differences. Additionally, seasonal categories were assigned as Spring (March, April, May 2011), Summer (June, July, August 2011), Fall (September, October, November 2010), and Winter (December 2010, January and February 2011). The same nonparametric multiple comparison analysis was performed on seasonal data for target analytes that were detected.

Variability and non-normality limited the ability to define site differences when individual UV-F compounds were analyzed. For each chemical, all detectable concentrations at each site were averaged for a given season (or annually) and then summed (Total UV-F). The data were \log_{10} transformed to examine the relationship between station and season (ANOVA and TUKEY HSD; JMP 11). Beach use and UV-F concentrations measured in the near-shore environment off the coast of SC were evaluated using regression analyses.

Of the seven target UV-F analytes, all but two (dioxybenzone and sulisobenzene) were detected during the sampling period (Table 2). The frequency of detection ranged from 8% to 100% for the remaining 5 UV-F chemicals. Padimate-O was not detected more than 33% of the time at any given station. Oxybenzone was the most commonly detected UV-F compound in this study being detected at every site and in 90% of the samples collected. Average annual frequency of detection for the remaining detected UV-F chemicals followed the trend avobenzene (60%), octinoxate (47%), octocrylene (38%) and padimate-O (15%) (Table 2). Average coastal concentrations from SC ranged from 9.94 ng/L (padimate-O) to 256 ng/L (oxybenzone). The maximum reported concentration in this study was for octocrylene (3730 ng/L at Site 5) (Table 2).

Mean UV-F concentrations were always greatest at Site 5 for all chemicals. Most often, the lowest mean UV-F concentrations were associated with Site 2 (octocrylene, oxybenzone and avobenzene). Mean concentrations at Site 6 and Site 4 were second or third highest for all

Table 1

Site descriptions detailing the typical beach use at each location.

Site	Short descriptor	Site description
Site 1	Myrtle Beach (MB)	Popular beach resort lined with hotel and other typical vacation amenities, tourist driven economy; multiple public beach access points (Myrtle Beach, SC)
Site 2	North Inlet (NI)	Located in North Inlet National Estuarine Research Reserve (NERR); served as the environmental reference site (Georgetown, SC)
Site 3	Coast Guard station (CG)	Northeastern most point on Folly Island, abandoned Coast Guard station with limited access (Folly Beach, SC)
Site 4	Wash out (WO)	Mostly residential, popular local beach with significant surfing/watersports use (Folly Beach, SC)
Site 5	Fishing pier (FP)	Local government run park with family amenities and adjacent hotel (Folly Beach, SC)
Site 6	County park (CP)	Southwestern most point on Folly Island, local government run park with access for up to 200 vehicles; includes amenities for daily beach use (Folly Beach, SC)

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