

Baseline

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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 (avobenzone, dioxybenzone, octocrylene, octinoxate, oxybenzone, padimate-o and sulisobenzone). 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 sulisobenzone/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 agrochemical 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), sulisobenzone (benzophenone-4), avobenzone, 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-methylbenzlidene 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

Table 1

Site description	s detailing	the typical	beach use	at each	location
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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)	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)

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 µL/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, sulisobenzone, and padimate-O; 1 ng/L for avobenzone; 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 log₁₀ 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 sulisobenzone) 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 avobenzone (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 avobenzone). Mean concentrations at Site 6 and Site 4 were second or third highest for all



Fig. 1. Station locations sampled along the South Carolina coastline.

compounds except for padimate-O, where mean concentrations at Site 6 were the lowest reported (not detected; Table 2).

Limited marine concentrations have been reported in the literature and the most directly relatable published concentrations are reported for oxybenzone and octinoxate in seawater at 8.2 and 10.7 ng/L, respectively (Giokas et al., 2005). Freshwater concentrations for avobenzone, octinoxate and octocrylene were reported in lakes in Switzerland at concentrations up to 28 ng/L (Poiger et al., 2004). Oxybenzone was reported at concentrations up to 125 ng/L in the same study (Poiger et al., 2004). Other publications detail UV-F concentrations as high as 7800 ng/L (oxybenzone) and 19000 ng/L (octinoxate) in waste water influent (Balmer et al., 2005). Waste water effluent concentrations were reported by Li et al. (2007) for octinoxate and octocrylene up to 116 and 153 ng/L, respectively, indicating significant reduction in concentrations during waste water treatment and processing. Poiger et al. (2004) showed similar reductions of oxybenzone where effluent concentrations were reported at levels up to 690 ng/L. These results indicate that waste water processing can efficiently reduce UV-F

Table 2

Summary of detection frequency, beach count and concentrations of UV-F based on site (all concentrations are ng/L; Ave = average; NR = not reportable).

	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	SC averages
	MB	NI	CG	WO	FP	СР	(All sites included)
Detection frequency of any compound (%)	57%	38%	42%	55%	67%	55%	52%
# of months collected	12	11	13	13	13	13	12.5
Beach count annual average (#)	16	0	8	15	82	49	28.3
Beach count range (#)	1-58	0	0-20	0–75	0-270	0-330	0.00
Count fall ave (#)	6	0	9	8	51	28	17.0
Count winter ave (#)	6	0	2	1	7	6	3.67
Count spring ave (#)	23	0	5	7	58	30	20.5
Count summer ave (#)	32	0	16	45	218	160	78.5
Average total UV-F	327	118	192	530	1670	922	626
Minimum total UV-F	0.350	0	0	0	0.50	0	
Maximum total UV-F	1287	454	744	3634	7806	3093	
Oxybenzone							
Annual average concentration	135	37.6	71.8	201	591	497	256
Concentration range	NR-575	NR-138	NR-467	NR-1766	NR-2203	NR-2126	
Frequency for site (%)	91	89	92	83	83	100	89.7
Spring average concentration	52	69	8	9	139	294	95.0
Summer average concentration	329	34	233	787	1533	1264	696.6
Fall average concentration	168	NR	42	4	688	428	221
Winter average concentration	3	33	4	3	5	3	8.54
Avobenzone							
Annual average concentration	52.7	31.9	34.9	79.3	234	88.5	86.9
Concentration range	NR-425	NR-158	NR-138	NR-366	NR-1298	NR-303	
Frequency for site (%)	45	56	42	75	75	67	60.0
Spring average concentration	13	1	34	22	181	44	49.3
Summer average concentration	160	71	69	235	597	173	217
Fall average concentration	1	19	36	53	151	132	65.4
Winter average concentration	21	18	NR	7	5.7	5	9.32
Octocrylene							
Annual average concentration	119	8.58	41.1	194	711	290	227
Concentration range	NR-382	NR-77	NR-311	NR-1375	NR-3730	NR-1060	
Frequency for site (%)	55	11	42	33	42	42	37.5
Spring average concentration	72	NR	NR	25	353	158	101
Summer average concentration	261	26	162	745	2016	878	681
Fall average concentration	156	NR	3	5	473	123	127
Winter average concentration	NR	NR	NR	NR	NR	NR	0.00
Octinoxate							
Annual average concentration	10.7	28.9	41.6	55.6	96.9	46.3	46.7
Concentration range	NR-35	NR-140	NR-235	NR-172	NR-438	NR-154	
Frequency for site (%)	18	44	33	58	67	58	46.3
Spring average concentration	8	22	21	9	24	19	17.2
Summer average concentration	12	55	37	96	166	44	68.3
Fall average concentration	0.35	NR	108	108	187	105	84.6
Winter average concentration	19	17	NR	9	11	18	12.4
Padimate_0							
Annual average concentration	9 57	10.9	2 35	0 129	36.7	NR	9 94
Concentration range	NR_104	NR_77	NR_28	NR_1 55	NR_101	NR	5.54
Eroquoncy for site (%)	19	22	0	Q	25	ND	15.2
Spring average concentration	NR	NR	NR	NR	NR	NR	0.00
Summer average concentration	25	28	0	ND	110	NR	30.00
Fall average concentration	0.53	NP	NR	0.52	27	NR	634
Minter average concentration	0.55	5	ND	0.32 ND	J/ ND	ND	0.04
winter average concentration	0.23	ن	1417	141	1111	1111	0.31

concentrations (>90% in these studies). Contained water (such as that found in swimming pools) concentrations are generally greater than those found in open environmental waters. Lambropoulou et al. (2002) reported values from swimming pools for oxybenzone of 2400 ng/L, octocrylene of 3300 ng/L and padimate-O of 2100 ng/L. The highest UV-F concentrations reported by Lambropoulou et al. (2002) were during the months where sunscreen use was higher and the magnitude was similar to the targeted compounds in the present study [oxybenzone (2203 ng/L) and octocrylene (3730 ng/L)], indicating that even in open waters, local dilution is not immediate, increasing the chances of exposure to higher concentrations.

Season plays an important role in UV-F monitoring. Mean UV-F concentrations were consistently highest in summer (Table 2) except for octinoxate, where summer concentrations were slightly less than average fall concentrations (Fig. 2; Table 2). A nonparametric comparison for each seasonal pair described pairwise differences among season for each UV-F (Table 3). Significant differences were regularly observed during the summer for UV-F concentrations of the 4 of the 5 detected compounds (octinoxate was the exception). Summer was by far the season where significant seasonal differences were most often observed. Fall patterns were generally similar to the differences seen between summer concentrations and those UV-F concentrations measured during the other seasons (Table 3).

Baron et al. (2013) evaluated UV-F concentrations in coastal areas of Chile and Colombia, including a variable defining Total UV-F to capture the cumulative UV-F concentration in coastal sediments. Four UV-F chemicals detected in the present study matched those used by Baron et al. (2013) with the exception being avobenzone. Summing concentration data for each of the UV-F chemicals from this study, average Total UV-F concentrations ranged from 118 ng/L (Site 2; minimal



Fig. 2. The average UV-F concentrations (+ the standard error) for each chemical across the four seasons.

beach use) to 1670 ng/L (Site 5; more extensive recreational beach use). Maximum Total UV-F concentrations ranged from 454 ng/L (Site 2) to 7806 ng/L (Site 5) (Table 2). There was no significant difference among sites when annual Total UV-F data (analyzed as Log10(TotalUV-F + 1)) was analyzed (ANOVA, Prob > F = 0.0925); although the average Total UV-F at Site 5 (FP) was nearly twice the next Total UV-F average concentration (Site 6, CP) (Fig. 3).

Similar analysis using season specific Total UV-F data resulted in significant site differences within Winter and Summer seasons (Fig. 4). An all pairwise comparison showed that during the Summer (Prob > F = 0.0082), Site 2 (the coastal reference location) was significantly different from Sites 4, 5 and 6 where weekend beach use was highest. Site 5 was also different from Sites 1 and 3. Additionally, Site 6 was also significantly different from Sites 1 and 3. During the Winter (Prob > F = 0.0325), Site 2 was different from Site 3.

Table 3

Seasonal multiple pairwise comparisons of individual organic UV filter concentrations using non-parametric comparison for each pair using Wilcoxon Method. P-values less than 0.05 were considered to be a significant difference and are bolded on the table.

Oxybenzone	Spring	Summer	Fall
Winter	0.631	<0.0001	0.226
Summer		0.0002	0.470
Avobenzone	Spring	Summer	Fall
Winter	0.197	<0.0001	0.0067
Spring		0.0009	0.111
Summer			0.0487
Octinoxate	Spring	Summer	Fall
Winter	0.732	0.124	0.0021
Spring		0.226	0.0039
Summer			0.136
Octocrylene	Spring	Summer	Fall
Winter	0.0158	<0.0001	0.016
Spring		0.0009	0.515
Summer			0.0054
Padimate-o	Spring	Summer	Fall
Winter	0.176	0.0783	0.469
Spring		0.0112	0.0620
Summer			0.300

Beach count data was regressed against Total UV-F and a positive relationship was observed ($R^2 = 0.5625$; Fig. 5). Additionally, positive relationships were observed for each season as well with R^2 equaling 0.034, 0.430, 0.724 and 0.889 for Winter, Summer, Fall and Spring, respectively (Fig. 6). Similarly, a seasonal trend was observed when season was regressed *versus* beach count. Sampling events in the summer were associated with high counts of people at the beach and were found to be significant when comparing average summer count data to the remaining seasons (Table 2). Warm weather brings increased recreational usages of bodies of water such as pools and lakes as well as increased application of sunscreen products (Esbenshade et al., 2010) and, as one would expect, led to maximum concentrations being measured during the summer season when sunscreen application was at its daily peak (Giokas et al., 2007).

Concentrations of UV filters found in coastal SC water samples were comparable to other studies. However, concentrations detected in the summer and fall months in the present study were more comparable to wastewater influent and effluent and shower water waste rather than seawater (Díaz-Cruz et al., 2008). Although effects of individual UV filters has been found at concentrations higher than those currently measured in the present study, it is possible that rapid accumulation and temporal effects at environmentally relevant concentrations play a part in the unknown environmental risk associated with UV filters, as well as their transformed chemical derivatives. To our knowledge, this assessment of sunscreens in the coastal environment was a first baseline study in coastal US waters and has provided insight into how coastal beach use relates to the occurrence of organic sunscreen chemicals. Patterns were observed in regards to the occurrence of the target analytes based both on beach use as well as seasonality. Monitoring the presence and quantities of anthropogenic chemicals, along with understanding the potential fate of the compound in the aquatic environment, may allow for a more responsible approach for planning and management of beach and coastal water use as well as marine protected areas and national marine sanctuaries alike.

Disclaimer

The scientific results and conclusions, as well as any opinions expressed herein, are those of the author(s) and do not necessarily



Fig. 3. Annual stacked data that represents the average Total UV-F measured at each site.

reflect the views of NOAA or the Department of Commerce. The mention of any commercial product is not meant as an endorsement by the Agency or Department. like to thank Pete Key, Jared Ragland, and Emily Pisarski for assistance and insightful review in the preparation of this manuscript.

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Fig. 4. Seasonal stacked data that represents the Total UV-F measured at each site.



Fig. 5. Regression describing the relationship between beach count and total UV-F concentration (total UV-F = 15.84 beach_count + 150.63; $r^2 = 0.5625$).

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Fig. 6. Regressions describing the relationships between beach count and total UV-F concentrations by season.

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