UV Filters and Tourism: Their Impact On The Environment

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1. Background

- Ultraviolet (UV) filters are widely used in cosmetics, sunscreens, and plastics to block UV radiation from the sun.
- Parabens are common ingredients in sunscreen formulation and thus are included in the list of target analytes. They are used as preservatives and anti-bacterial agents.
- Studies show that some UV filters and parabens demonstrate estrogenicity and multiple hormonal activities *in vitro*[1].
- Potential impact of these materials on the environment and human health is of great concern.
- Because of the high consumption volume and high lipophilicity of many UV filters, these compounds have the potential to enter and persist in the environment and to bioaccumulate in tissues of living organisms.
- People from all over the world visit Las Vegas, bringing with them their own medications and personal care products (e.g., cosmetics, sunscreens).
- Use of these materials contributes loading in the environment.
- To date, there are only 15 U.S. FDA-approved, organic UV filters, while European countries, Australia, and Japan sanction additional compounds[2].

2. Purpose of Current Work

- Develop methods to monitor the presence of UV filters and parabens in wastewater treatment plant effluent and other environmental compartments.
- Monitor and evaluate potential sources of and temporal variation in the occurrence of these chemicals.
- Determine if certain chemical loadings can be used as indicators of tourist influx in the Las Vegas Valley.

Figure 1. Map of Las Vegas Valley and locations of wastewater treatment facilities.

Figure 2. Clark County Water Reclamation District (CCWRD)collects and reclaims an average of 100 MGD[3] of wastewater from its service area (shaded in pink in the unincorporated portions of Clark County within the Las Vegas Strip, plus the communities of Blue Diamond, Laughlin, Indian Springs, Overton and Searchlight.

3. Experimental

- Water samples are going to be collected from effluent of the Clark County Reclamation District in-situ thru SPE cartridges (Biotage Evolut® ABN and Waters Oasis® HLB, 1g).
- Solvent elution of analytes were performed using FMS Solid Phase Extraction (SPE) system.
- All HPLC-MS/MS analyses were performed using a Thermo Finnigan (San Jose, CA) HPLC Surveyor® interfaced to a Thermo Finnigan TSQ Quantum Ultra AM® triple quadrupole mass spectrometer (AM3QMS).
- Analytical separation column was a Pursuit® diphenyl, 3.5-µm particle size, 2.1-mm x 150-mm column (Varian Inc., Walnut Creek, CA) housed in an oven at 30°C. The mobile phase at 200 µL/min consisted of 0.5% acetic acid, 100% acetonitrile, and 100% methanol in gradient elution. Methanol was introduced at constant flow rate of 10% of the total flow.
- All GC-MS analyses were performed with a Varian 3800 capillary gas chromatograph and 320 mass spectrometer (Varian, Inc, Walnut Creek, CA) using electron ionization and single-ion monitoring (SIM) mode. The gas chromatograph was fitted with a 30-m x 0.25-mm ID fused silica capillary column coated with a 0.10-µm film of crossbonded 5% phenyl - 95% methyl polysiloxane (DB-5HT, J&W Scientific, Folsom, CA). The injector temperature was at 250°C. A pulsed pressure of 174 kPa (25 psi) was applied during injection and held for 0.75 min. After the initial pressure pulse, the carrier gas flow was held constant at 1 mL min-1. The initial oven temperature was 60°C held for 1 min, ramped at 30°C min-1 to 150°C, then to 290°C at 8°C min-1 and and held for 3.0 min (total chromatographic time = 24.5 min).

Instrumentation

Figure 3. FMS SPE system

Figure 4. Varian 3800 GC and 320 MS

Figure 5. Thermo Finnigan HPLC Surveyor® coupled with Thermo Finnigan TSQ Quantum Ultra AM® triple quadrupole mass spectrometer

4. Results

Compound Chemical Formula (Molecular Weight)	CAS Reg. No.	Collision Energy (V)	Precursor Ion LC-MS/MS / GC-MS	Product Ion LC-MS/MS / GC-MS	LC-MS/MS Retention Time	GCMS Retention Time	Country Permitted in
Phenyl salicylate $C_{13}H_{10}O_3$ (214)	118-55-8	18 18	213 (M-H)⁻ 215 (M+H)⁺	93 (C6H5O)⁻ 121 (C6H5COO)⁺		8.275	
			121	214, 93, 65			
Benzylsalicylate $C_{14}H_{12}O_3$ (228)	118-58-1	20 18	227 (M-H)⁻ 229 (M+H)⁺	93 (C6H5O)⁻ 151 [(M+H)-C6H6]⁺		9.544	
			91	228, 92, 65			
2-Ethylhexyl salicylate $C_{15}H_{22}O_3$ (250)	118-60-5	22	249 (M-H)⁻	137 [(M-H)-C8H16]⁻		8.89	EC, USA, AUS, JP, PRC, CAN, RSA, ROK
			120	138, 121, 250			
p-Aminobenzoic acid (PABA) $C_7H_7NO_2$ (137)	150-13-0	19 19	136 (M-H)⁻ 138 (M+H)⁺	92 [(M-H)-CO2]⁻ 77 (C6H5)⁺			EC, USA, AUS, JP, PRC, CAN, SAf, ROK
Homosalate (3,3,5-Trimethylcyclohexyl salicylate) $C_{16}H_{22}O_3$ (262)	118-56-9	21	261 (M-H)⁻	137 (C7H5O3)⁻		9.484	EC, USA, AUS, JP, CAN, PRC, RSA, ROK
			138	109, 120, 262			
Oxybenzone (Benzophenone-3) (2-Hydroxy-4-methoxybenzophenone) $C_{14}H_{12}O_3$ (228)	131-57-7	22 20	227 (M-H)⁻ 229 (M+H)⁺	211 [(M-H)-CH4]⁻ 151 [(M+H)-C6H6]⁺	15.75		EC, USA, AUS, JP, CAN, CHI, RSA, ROK
			227	151, 228, 77			
Ecamsule/Mexoryl SX (Terephthalylidene dicamphor sulfonic acid) $C_{28}H_{34}O_8S_2$ (562)	90457-82-2	27	280 $(M-2H)^{2-}$	437 $(M-2H- SO_3 -C_3H_7)^-$	10.54		EC, USA, AUS, JP, CAN, PRC, RSA
2-phenyl-5-benzimidazole-sulfonic acid (Ensulizole) $C_{13}H_{10}N_2O_3S$ (274)	27503-81-7	28 31	273 (M-H)⁻ 275 (M+H)⁺	193 [(M-H)-SO3]⁻ 194 [(M+H)-SO3H]⁺	2.94		EC, USA, AUS, JP, CAN, PRC, RSA, ROK
4-Hydroxy benzoic acid-C6 $C_7H_6O_3$ (144)		16	143 (M-H)⁻	99 [(M-H)-COO]⁻	3.24		
4-4'-dihydroxybenzophenone $C_{13}H_{10}O_3$ (214)	611-99-4	33 22	213 (M-H)⁻ 215 (M+H)⁺	93 (C6H4OH)⁻ 121 $[(M+H) – C_6H_5OH]^+$	5.38	14.362	
			121	214, 93, 70			
Methylparaben $C_8H_8O_3$ (152)	99-76-3	20	151 (M-H)⁻	92 $(C_6H_4O)^-$	5.35	5.742	
			121	152, 93, 65			
Methyl paraben-C6 (158)		21	157 (M-H)⁻	98 $(C_6H_4O)^-$	5.37	6.1	
			127	158, 99			
Benzophenone-2 (2,2',4,4'-Tetrahydroxybenzophenone) $C_{13}H_{10}O_5$ (246)	131-55-5	19 13	245 (M-H)⁻ 247 (M+H)⁺	135 [(M-H)-C6H6O2]⁻ 137 [(M+H) -C6H6O2]⁺	6.8		AU, JP, RSA
Benzophenone-4 (Sulisobenzone) (2-Hydroxy-4-methoxybenzophenone-5-sulfonic acid) $C_{14}H_{12}O_6S$ (308)	4065-45-6	32	307 (M-H)⁻	211 [(M-H)-SO3H-CH3]⁻	7.82		EC, USA, AUS, JP, CAN, PRC, RSA, ROK
Ethylparaben $C_9H_{10}O_3$ (166)	120-47-8	21	165 (M-H)⁻	92 $(C_6H_4O)^-$	7.25	6.253	
			121	166, 138, 93			
2,4,4'-trihydroxybenzophenone $C_{13}H_{10}O_4$ (230)	1470-79-7	26 18	229 (M-H)⁻ 231 (M+H)⁺	93 (C6H5O)⁻ 129	7.76	15.46	
			137	230, 121, 229			
Propylparaben $C_{10}H_{12}O_3$ (180)	94-13-3	22	179 (M-H)⁻	92 $(C_6H_4O)^-$	10.06	7.075	
			121	138, 93, 180			
4-hydroxybenzophenone (metabolite) $C_{13}H_{10}O_2$ (198)	1137-42-4	34 19	197 (M-H)⁻ 199 (M+H)⁺	92 [(M-H)-C6H5CO]⁻ 121 $[(M+H)-C_6H_6]^+$	10.41	10.986	
			121	198, 77, 105			
n-Butyl paraben-C6 (200)		23	199 (M-H)⁻	98 $(C_6H_4O)^-$	12.19	8.03	
			127	144, 200			
Butylparaben $C_{11}H_{14}O_3$ (194)	94-26-8	22	193 (M-H)⁻	92 $(C_6H_4O)^-$	12.19	8.032	
			121	138, 194, 93			
Benzophenone-1 (2,4-Dihydroxybenzophenone) $C_{13}H_{10}O_3$ (214)	131-56-6	28 21	213 (M-H)⁻ 215 (M+H)⁺	91 (C6H3O)⁻ 137 [(M+H)-C6H6]⁺	12.45	12.032	JP, RSA
			137	213, 214, 77			
Benzylparaben $C_{14}H_{12}O_3$ (228)	94-18-8	20	227 (M-H)⁻	92 $(C_6H_4O)^-$	13.39	12.275	
			121	91, 228, 65			
3-(4-Methylbenzylidene) camphor $C_{18}H_{22}O$ (254)	36861-47-9	18	255 (M+H)⁺	212 [(M+H)-C3H7]⁺	18.14	11.527	EC, USA, AUS, CAN, PRC, RSA, ROK
			254	128, 171, 211			
Menthyl anthranilate $C_{17}H_{25}NO_2$ (275)	134-09-8	11	276 (M+H)⁺	138 [C6H4(COOH)NH3]⁺	19.4	12.156	USA, AUS, CAN, RSA, ROK
			137	119, 120, 275			
Octyldimethyl PABA (2-Ethylhexyl-4-dimethylaminobenzoate) $C_{17}H_{27}NO_2$ (277)	21245-02-3	25	278 (M+H)⁺	166 $[(M+H)-C_8H_{16}]^+$	19.43	13.698	EC, USA, AUS, JP, CAN, PRC, RSA, ROK
			165	164, 148, 277			
Octyl methoxycinnamate $C_{18}H_{26}O_3$ (290)	5466-77-3	9 15	291 (M+H)⁺ 289 (M-H)⁻	179 $[(M+H) – C_8H_{16}]^+$ 229	19.56	14.199	EC, USA, AUS, JP, CAN, PRC, RSA, ROK
			178	161, 290, 177			
Octocrylene (2-Ethylhexyl-2-cyano-3,3 diphenylacrylate) $C_{24}H_{27}NO_2$ (361)	6197-30-4	12	362 (M+H)⁺	250 [(M+H)-C8H16-NH3]⁺	20.84	17.54	EC, USA, AUS, JP, CAN, PRC, RSA, ROK
			112	249, 204, 360			
Bis-(2-Ethylhexyl)adipate-C6 (376)		14	377 (M+H)⁺	135	20.97	14.59	
			135	153,112, 247			
Avobenzone (butyl methoxydibenzoylmethane) $C_{20}H_{22}O_3$ (310)	70356-09-1	20	**311** (M+H)⁺	135 $(C_8H_7O_2)^+$	17.37		EC, USA, AUS, JP, CAN, PRC, RSA, ROK

Note: Compounds highlighted in yellow are not amenable to LC. Compounds highlighted in green are not amenable to GC.
EC=European countries; USA=United States of America; AUS=Australia/New Zealand; JP=Japan; PRC=Peoples' Republic of China; CAN=Canada; RSA=Republic of South Africa; ROK=Republic of Korea

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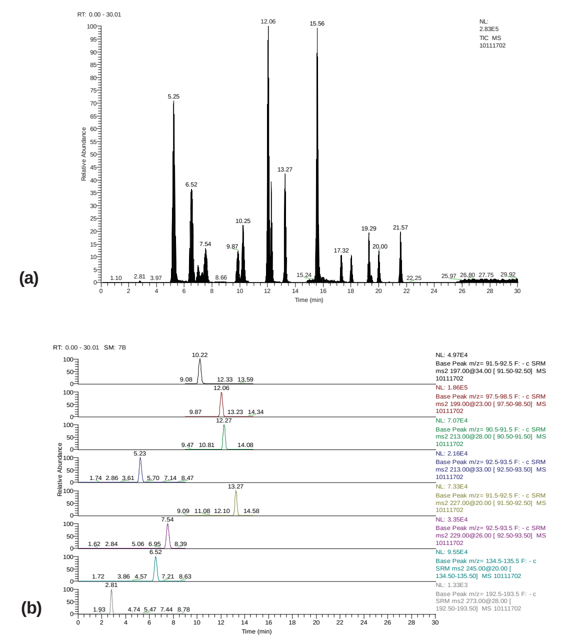

Figure 6. Total (a) and extracted (b) ion chromatogram of extract from spiked DI water.

- Both p-Amino benzoic acid and Mexoryl SX are problematic compounds for the current method used.
- Avobenzone produced two peaks, which is a result of compound transformation due to several solvents used for dissolution. A new batch of neat standard will be analyzed for confirmation.
- Initial recovery experiments in DI water gave the following preliminary results:

LC-MS/MS analysis:

Benzophenones: 82 - 156% Parabens: 31 – 45% Camphor: 52 -74%

Sulfonic acids: 0% except for Benzophenone-4, which was at 44-60% Esters: 0 – 17%

- Poor recovery of esters maybe due to hydrolysis.
- GC-MS analysis of same sample extracts as above generally resulted in lower recoveries as compared to LC-MS/MS analysis.

5. Conclusions & Future Work

- LC-MS/MS and GC-MS methods have been developed to identify sunscreen agents and parabens in solvent matrix.
- Two SPE materials (Biotage Evolut® ABN and Waters Oasis® HLB) are being evaluated for optimum recovery of target analytes.
- Extraction methods need to be optimized for maximum recovery of analytes.
- Water samples from the effluent of CCWRD main facility will commence this winter and will continue thru fall of next year.
- Water samples from the effluent of the City of Las Vegas Wastewater Treatment Facility will also be collected.
- Biosolids are considered as another matrix to sample in the near future.
- Research collaboration with CCWRD will be established to leverage resources.

References

[1] *Schlumpf, M., Cotton, B., Conscience, M., Haller, V., Steinmann, B. and Lichtensteiger, W. (2001). "In Vitro and in Vivo Estrogenicity of UV Screens " Environmental Health Perspectives 109(3): 239-244.*

[2] *Shaath, N. A. (2007). The Encyclopedia of Ultraviolet Filters. Shaath, N. A. Carol Stream, IL, Allured Publishing Corp.*

[3] http://www.cleanwaterteam.com/home.html.

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