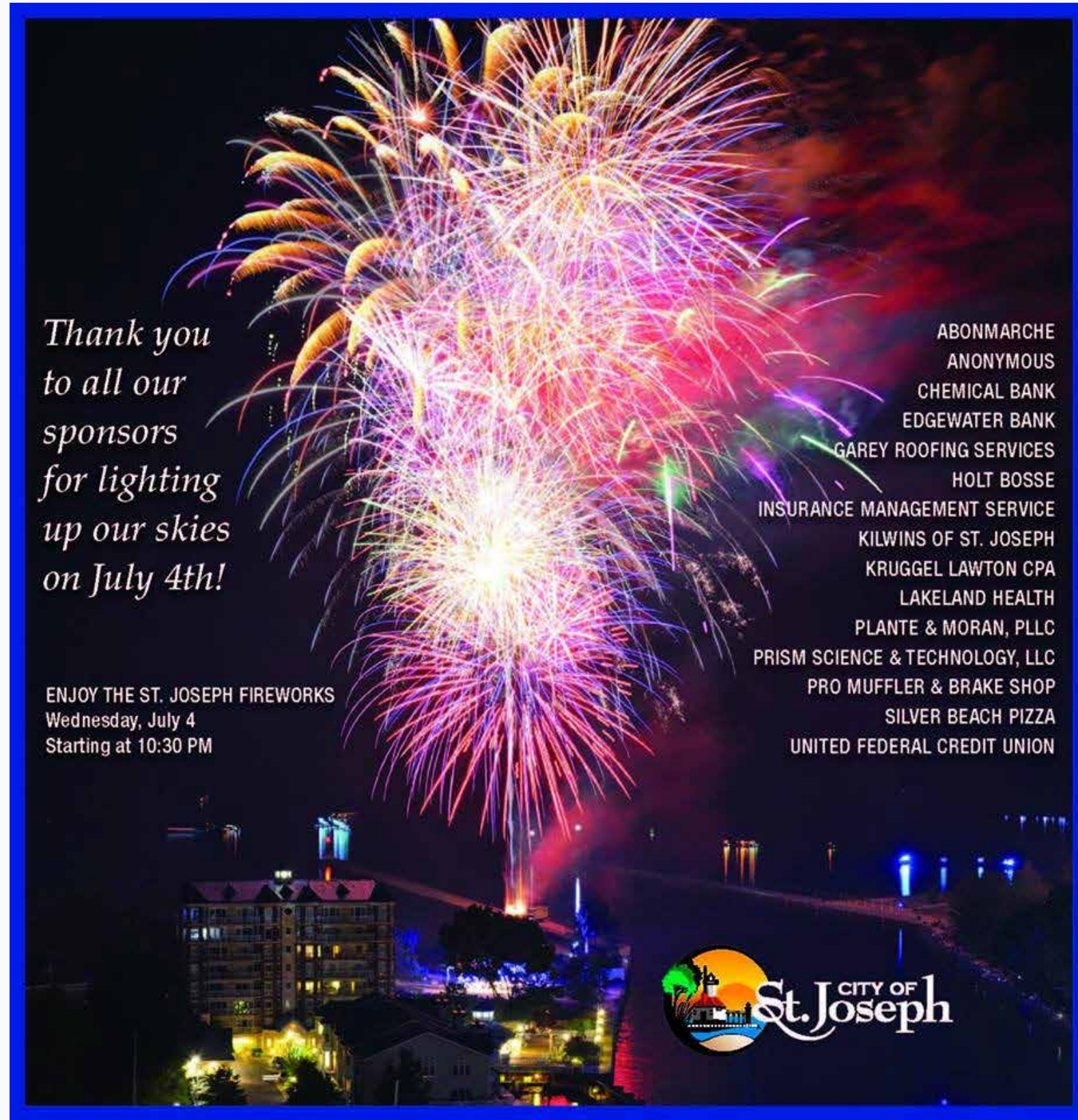


# Of Fireworks and Tourism: GCxGC-HRMS Analysis of Summer Impacts on Lake Michigan Water Quality

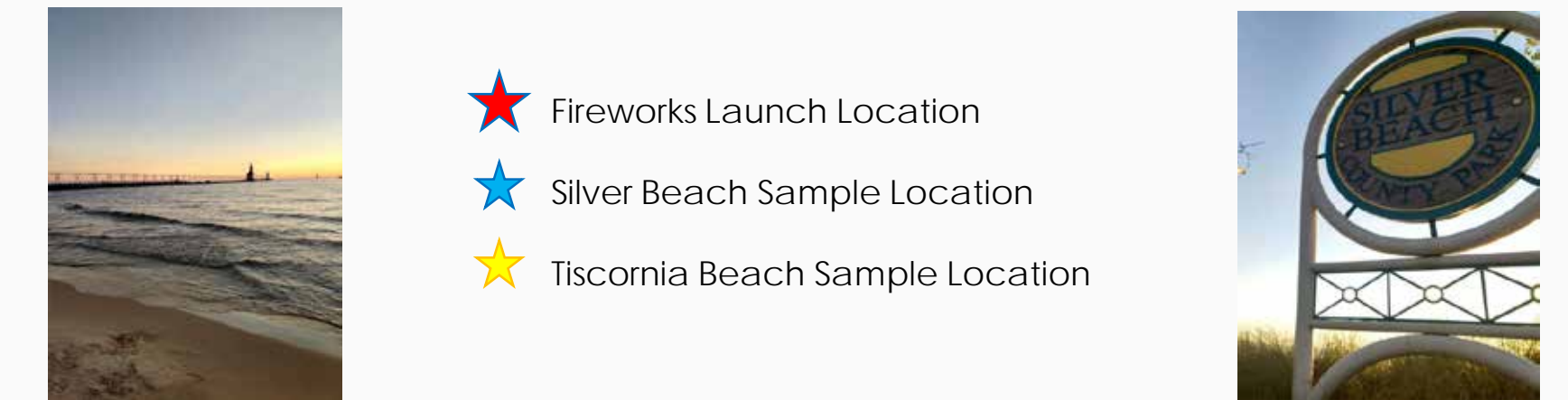
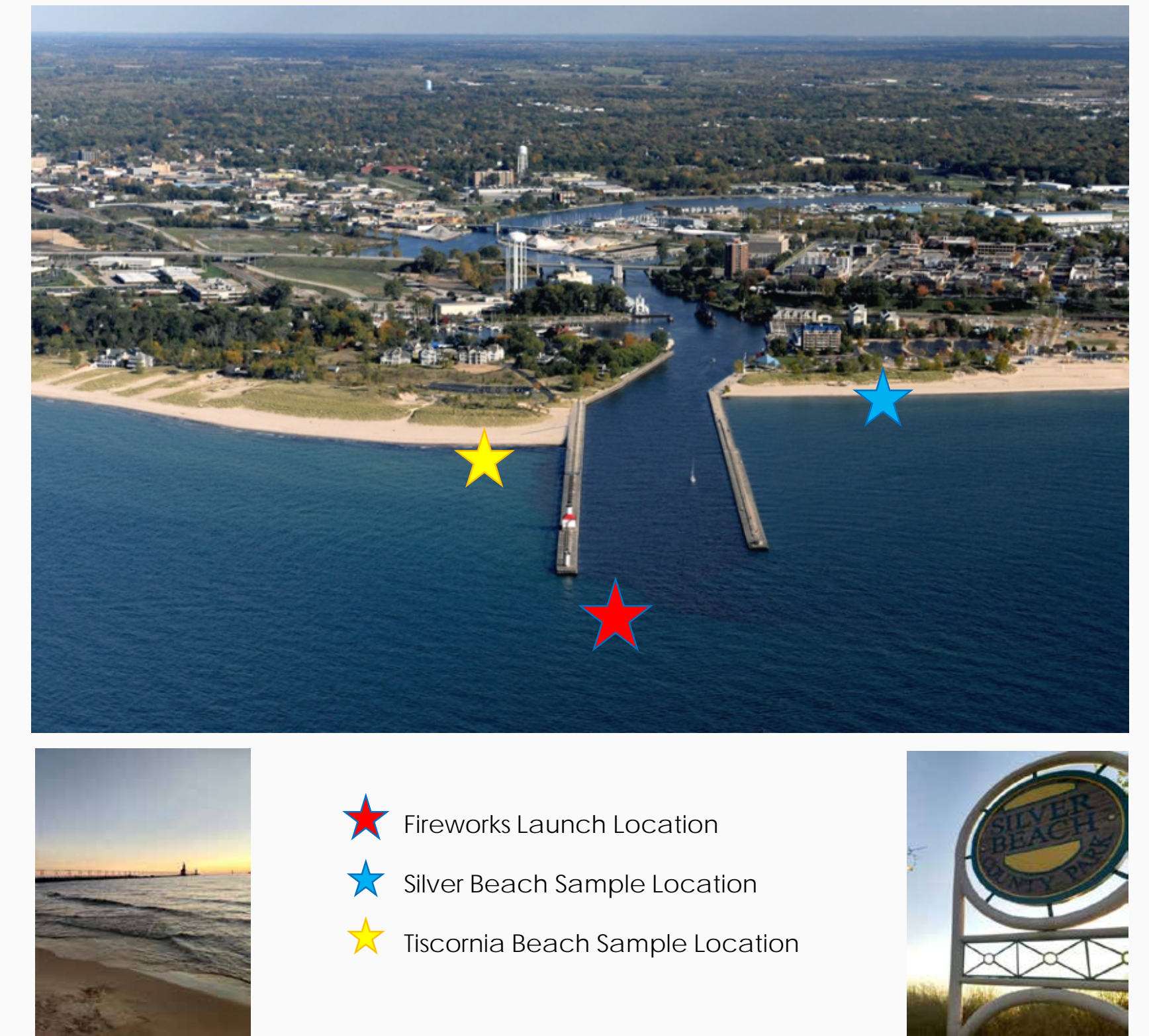
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## Overview

An estimated 16,000 fireworks displays are held in the United States each 4<sup>th</sup> of July to celebrate the national Independence Day holiday. The potential short-term environmental impacts of such displays is explored in this presentation, where samples of Lake Michigan water were collected from multiple locations before and after 4<sup>th</sup> of July fireworks were launched from a nearby pier. The influx of tourism to Lake Michigan beaches during this national holiday also contributes to measurably higher levels of chemicals that can be attributed to personal care products like sunscreen and insect repellent. Water samples are extracted via direct immersion using SPME Arrow, solid-phase microextraction fibers with increased stationary phase volumes, and analyzed with comprehensive two-dimensional gas chromatography coupled to high-resolution time-of-flight mass spectrometry (GCxGC-HRTOFMS). Full non-targeted analysis of the water samples clearly demonstrate the chemical differences between samples pre- and post-fireworks display, and pinpoint contributions to environmental pollution that occur as a result of the pyrotechnic displays and increased human traffic near the water sampling sites.

## Sample Collection

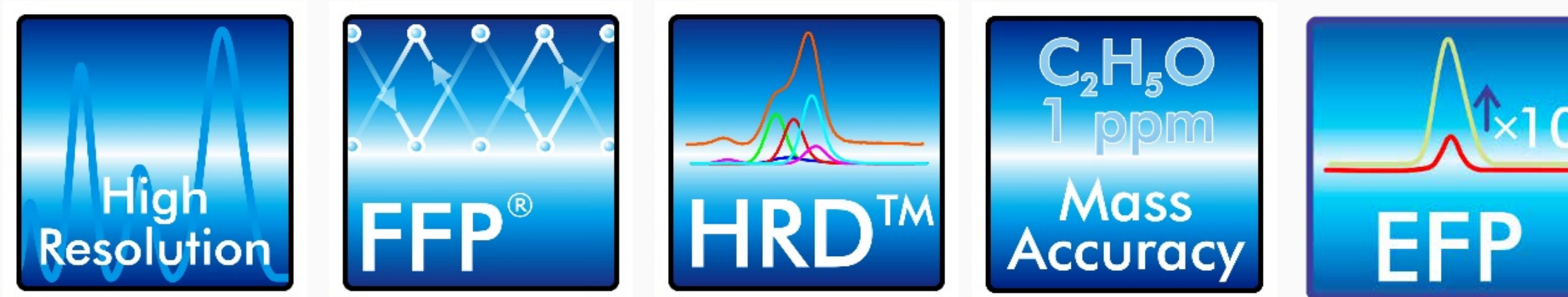


- 60 mL samples were collected at each beach on July 2<sup>nd</sup> and on July 4<sup>th</sup> (an hour after the fireworks show)
- pH was adjusted to 2 with HCl
- Samples were stored in freezer until analysis

## Analytical Parameters



Pegasus GCxGC-HRT+



## Comprehensive GCxGC

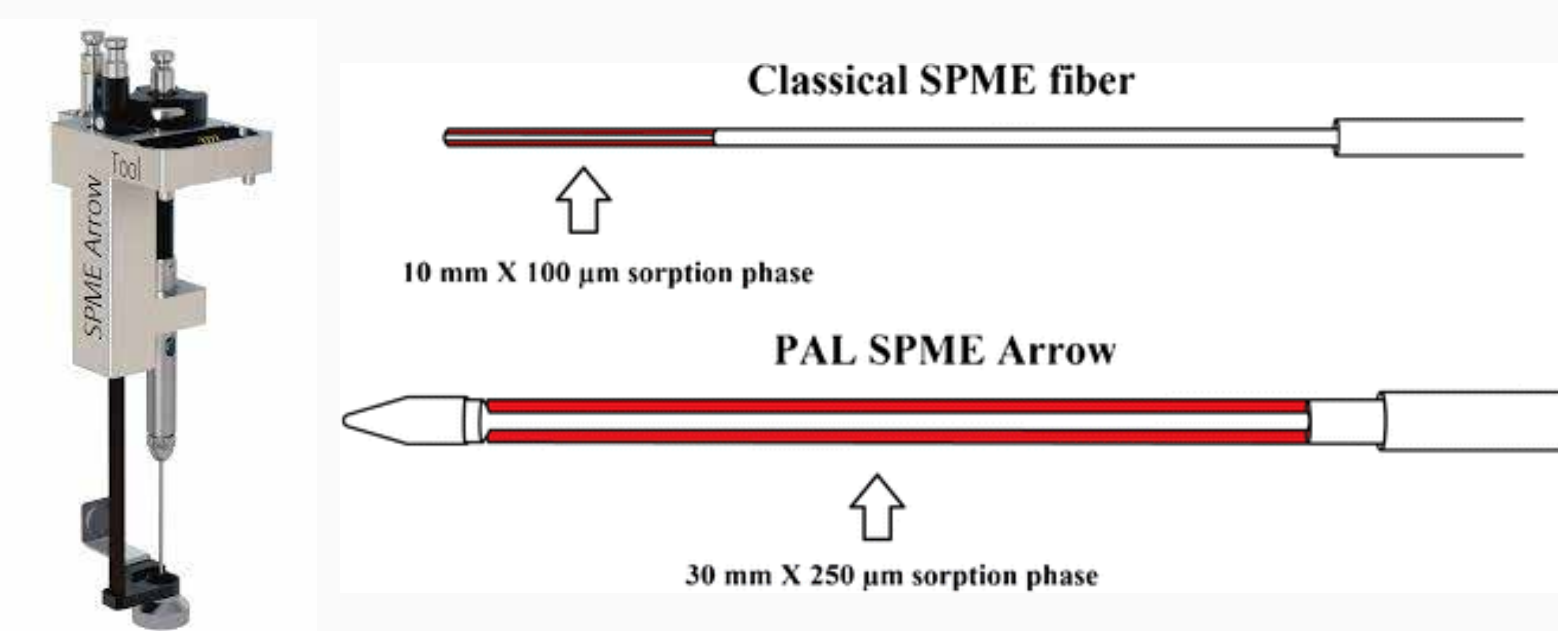
Gas Chromatograph	LECO Quad-Jet Thermal GCxGC
Injection	SPME Arrow, splitless @ 250 °C
Carrier Gas	He @ 1.4 mL/min, Corrected Constant Flow
Primary Column	Rxi-5ms, 30 m x 0.25 mm i.d. x 0.25 µm coating (Restek, Bellefonte, PA, USA)
Secondary Column	Rxi-17SIMS, 1.50* m x 0.25 mm x 0.25 µm coating *1.00 m coiled in 2 <sup>nd</sup> oven and 0.31 m in transfer line
Temperature Program	2 min at 40 °C, ramped 10 °C/min to 300 °C, hold for 5 min Secondary oven maintained +5 °C relative to primary oven Modulator maintained +15 °C relative to secondary oven
Modulation	5.0 s: 1.00 s hot pulse time
Transfer Line	320 °C

## High-Resolution Mass Spectrometry

Mass Spectrometer	LECO Pegasus HRT+ with EFP
Ion Source Temperature	250 °C
Mass Range	40-520 m/z
Acquisition Rate	200 spectra/s

## SPME Arrow

Use of SPME Arrow allowed for 10x increase of sorption volume over traditional SPME for capture of volatile and semi-volatiles in water, with a thicker, more robust fiber that decreased risk of breakage.

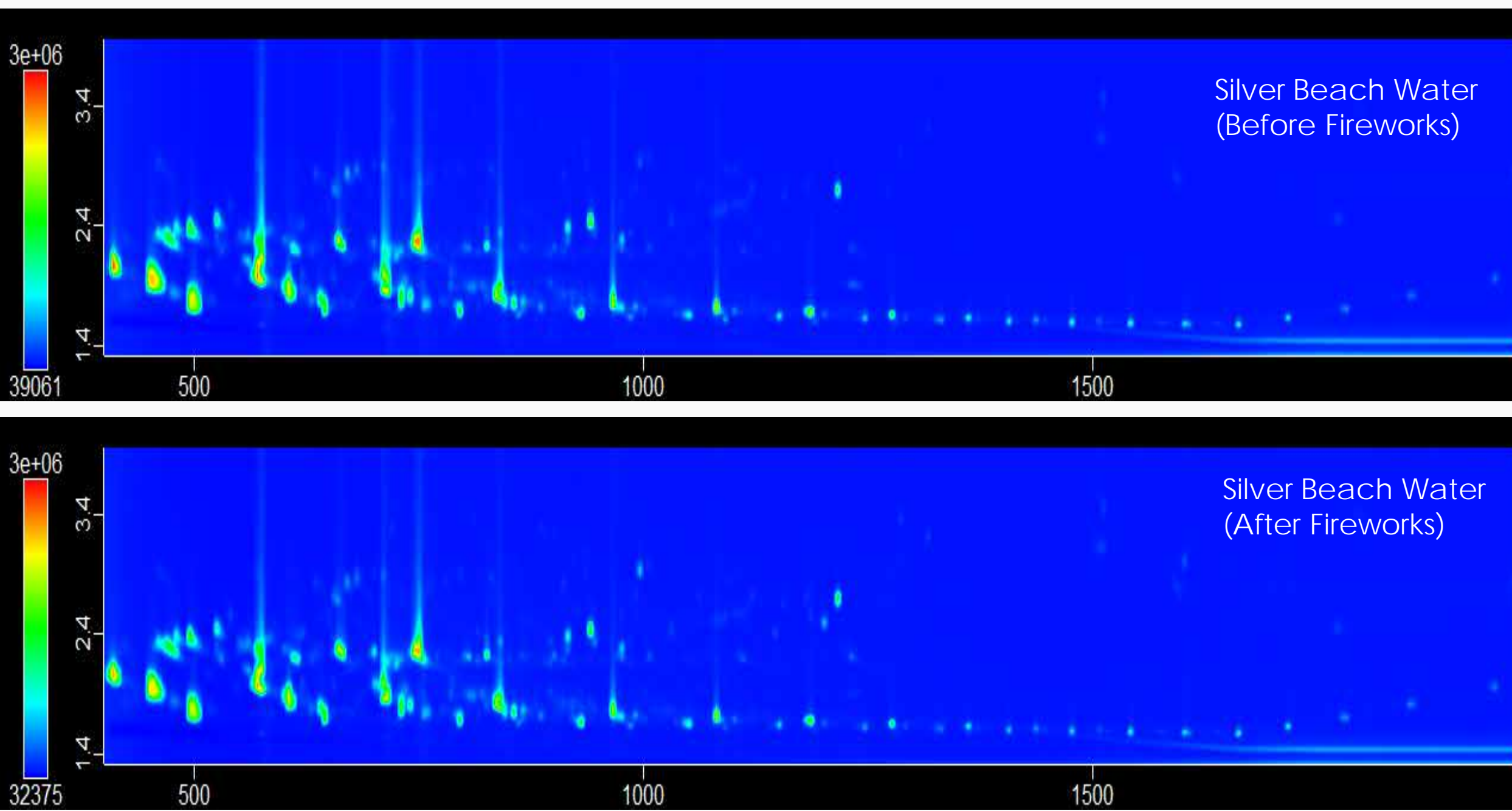


## SPME Arrow Immersion Parameters Used for Water Samples

Sorption Phase	1.5 mm DVB/Carbon WR/PDMS
Conditioning Temperature	270 °C
Conditioning Time	1 min
Stirrer Speed	1200 rpm
Extraction Temperature	30 °C
Extraction Time	30 min
Sample Desorb Time	2 min

## Results

### GCxGC TIC Contour Plots

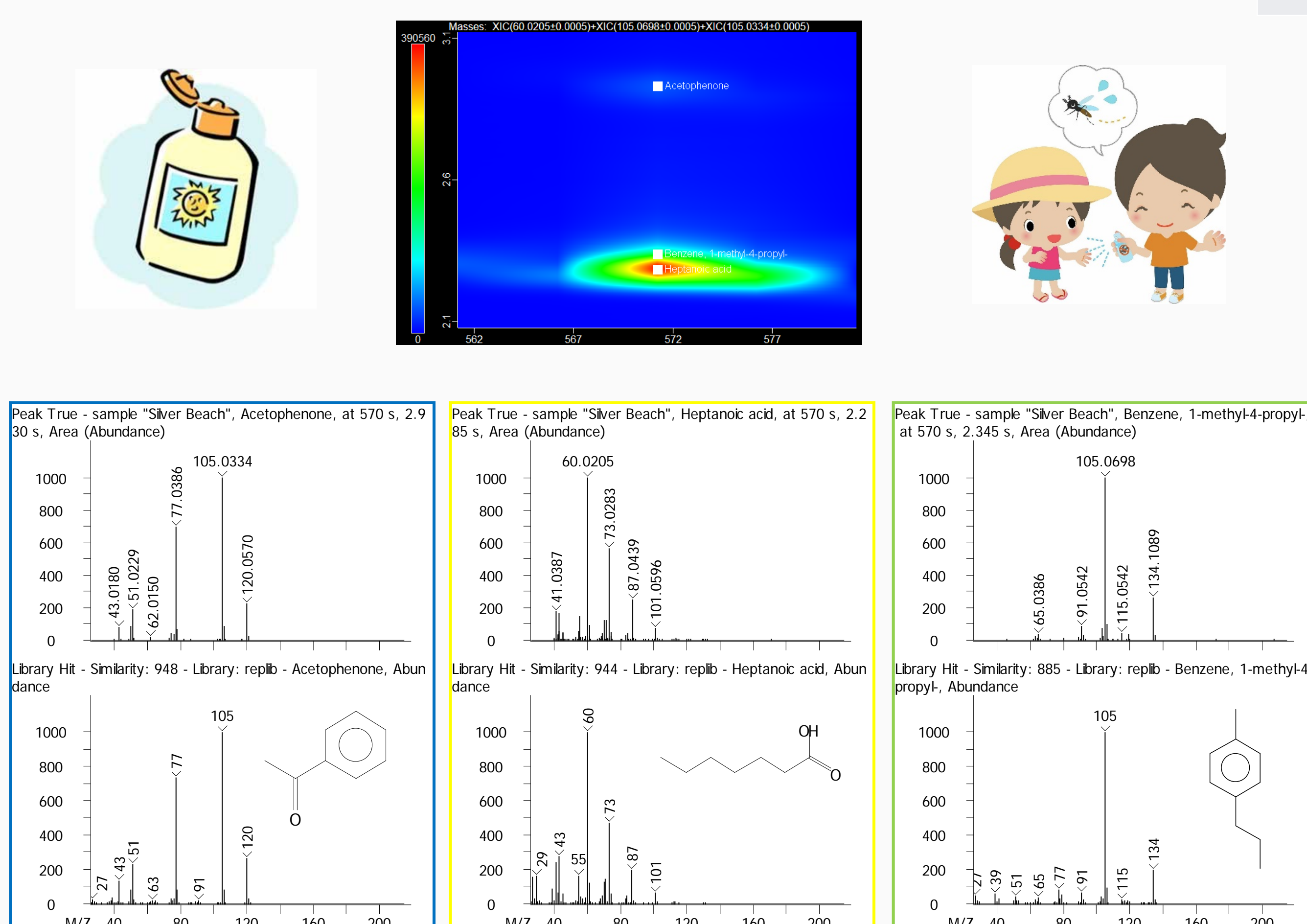


The contour plots above show a direct visual comparison of results from water samples collected at the Silver Beach location before and after the fireworks demonstration.

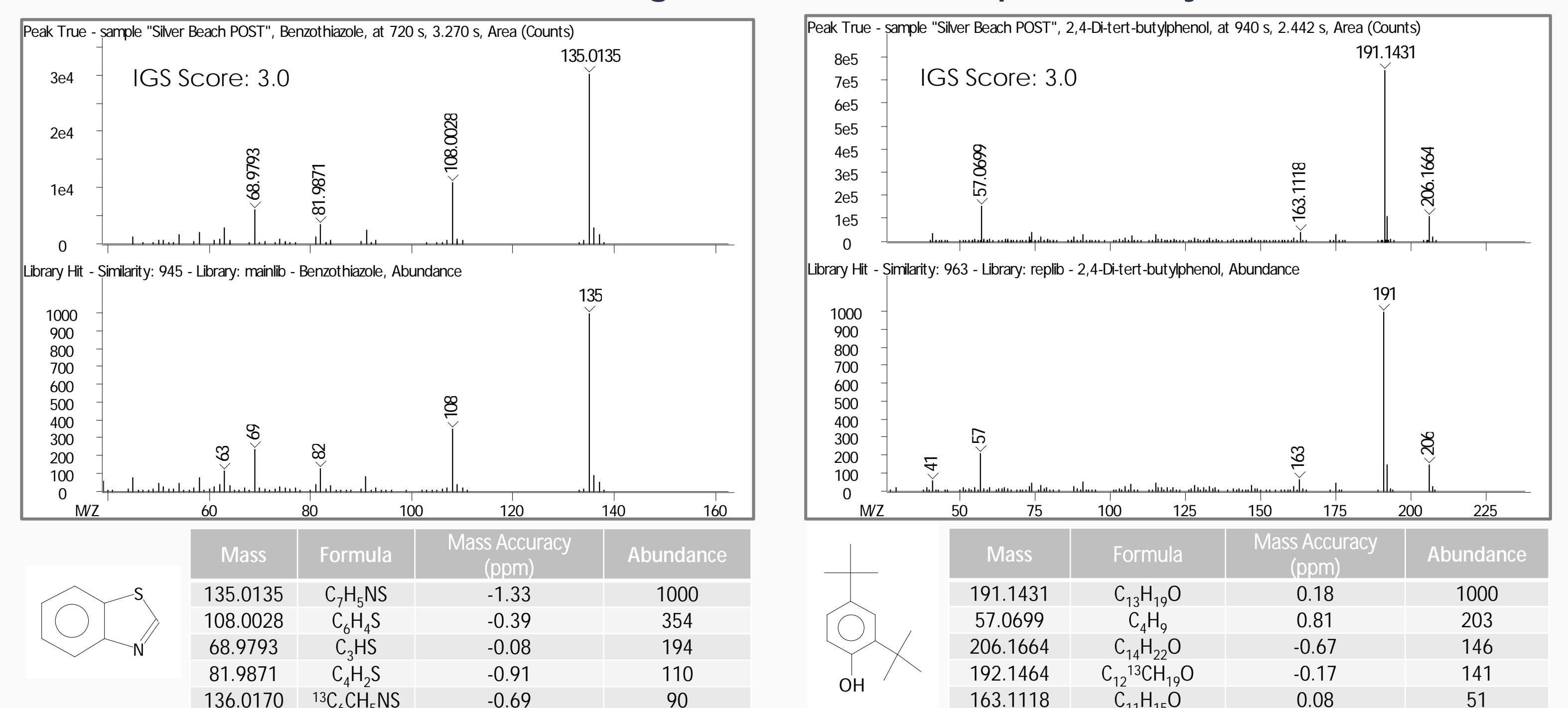
### Table of Identified Compounds of Interest

Compound of Interest	Formula	Similarity Score	Retention Time	Use	Change
Butyrolactone	C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	911	425 s, 3.485 s	lotion solvent	--
Benzeneacetaldehyde	C <sub>8</sub> H <sub>8</sub> O	857	545 s, 2.960 s	fragrance	--
Dibutoxymethane	C <sub>9</sub> H <sub>20</sub> O <sub>2</sub>	886	560 s, 2.105 s	emulsifier	slight increase
Octanoic acid	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	945	660 s, 2.285 s	pesticide	slight increase
Benzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	873	660 s, 2.689 s	insect bite treatment	4x increase
Methyl salicylate	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	934	690 s, 2.750 s	fragrance	slight increase
Benzothiazole	C <sub>7</sub> H <sub>5</sub> NS	945	720 s, 3.270 s	insecticide	slight increase
n-Decanoic acid	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	922	825 s, 2.230 s	fragrance	slight increase
δ-Nonalactone	C <sub>9</sub> H <sub>16</sub> O <sub>2</sub>	861	855 s, 3.000 s	coconut fragrance	newly present
Vanillin	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	839	860 s, 3.308 s	vanilla fragrance	newly present
Diisopropyl adipate	C <sub>12</sub> H <sub>22</sub> O <sub>4</sub>	929	895 s, 2.330 s	skin softener	10x increase
Dimethyl phthalate	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>	866	900 s, 3.190 s	insecticide	slight increase
2,4-Di-tert-butylphenol	C <sub>14</sub> H <sub>22</sub> O	963	940 s, 2.442 s	antioxidant	--
Diethyltoluamide	C <sub>12</sub> H <sub>17</sub> NO	925	995 s, 2.970 s	insecticide	5x increase
Diethyl Phthalate	C <sub>12</sub> H <sub>14</sub> O <sub>4</sub>	964	1005 s, 2.970 s	fragrance; hair conditioner	slight increase
N-n-Butylphthalimide	C <sub>12</sub> H <sub>13</sub> NO <sub>2</sub>	907	1055 s, 3.085 s	skin conditioner	newly present
γ-Dodecalactone	C <sub>12</sub> H <sub>22</sub> O <sub>2</sub>	905	1060 s, 2.710 s	peach/apricot/strawberry fragrance	newly present
2-Ethylhexyl salicylate	C <sub>15</sub> H <sub>22</sub> O <sub>3</sub>	908	1145 s, 2.410 s	UVB ray absorber	newly present
Homosalate	C <sub>16</sub> H <sub>22</sub> O <sub>3</sub>	922	1200 s, 2.495 s	sunscreen	40x increase
Oxybenzone	C <sub>14</sub> H <sub>12</sub> O <sub>3</sub>	923	1285 s, 3.360 s	sunscreen	newly present
Diethylene glycol dibenzoate	C <sub>18</sub> H <sub>18</sub> O <sub>5</sub>	959	1510 s, 3.455 s	hair conditioner	--
Octocrylene	C <sub>24</sub> H <sub>38</sub> O <sub>2</sub>	925	1600 s, 3.005 s	sunscreen	15x increase

## Benefits of GCxGC



## Benefits of High-Resolution Mass Spectrometry



High-resolution mass accuracy on the Pegasus HRT+ 4D yields excellent mass accuracies for both fragments and molecular ions that occur. Here, mass accuracies of less than 2ppm aid in confident identification of benzothiazole, a sulfur- and nitrogen-containing insecticide, and 2,4-Di-tert-butylphenol, a popular oxygenated sunscreen ingredient. Both compounds also scored a 3.0/4.0 (the best possible without retention indices) on the automated Identification Grading System (IGS), which compares not only library similarity scores, but also the presence of molecular ion, mass accuracies of major fragments, and retention indices when available.

## Conclusion

Although no direct chemical effects from fireworks were found in the water by this analysis method, SPME Arrow used in conjunction with GCxGC-HRTOFMS provided a wealth of information about increases in chemicals from personal care products due to increased human traffic near the waterfront, with confident identification of active ingredients from insect repellent, sunscreen, and a variety of summery fragrance compounds.

Use of GCxGC allows for separation in the second dimension of compounds that would otherwise coelute in one-dimensional GC, which can be seen in vertical bands of compounds like the one shown above. Here three distinct compounds were identified that shared the first dimension retention time. Because of the increase in chromatographic separation, better-quality deconvoluted spectra of these peaks could be generated for library matching and identification for acetophenone, heptanoic acid, and 1-methyl-4-propylbenzene.