Continuous Low-Level Aquatic Monitoring

C.L.A.M

AQUALYTICAL

C·I·Agent STORM·WATER SOLUTIONS

The Event

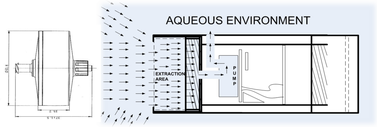
The Deep Water Horizon Event, injected millions of gallons of crude oil into the oceans water column. With the addition of dispersants, and surface burning, a question surfaced with the oil. What remained dissolved and suspended in the water column?

Crude oil and component PAH concentrations in the marine water column are extremely low, even after a spill event. In the past, estimations of PAH concentrations in the water column were obtained from mussel and fish tissue residue studies, using equilibrium partitioning calculations.

A direct, quantitative method and device was needed to establish these ultra trace levels of oil and toxic components in the water column. This would allow the monitoring of toxic loading of total and dissolved oil in different areas and depths in the water column, during and after the spill event.

The Device and Method

A submersible SPE extractive sampler was designed to meet these requirements.



CL.A.M. (Continuous Low-Level Aquatic Monitoring), The device draws water in-situ at low quantitative flow rates through SPE (Solid Phase Extraction) media disks, following EPA established SPE extraction procedures.

The ***C.L.A.M.*** is a submersible extraction sampler, using EPA approved SPE media to sequester Pesticides, Herbicides, PAH's, TPH, and other trace organics from water.

The ***C.L.A.M.*** provides an extraction event that can be hours, days or weeks long, allowing capture of trace pollutants from illicit and episodic events.

The ***C.L.A.M.*** actually extracts the water in-situ, with the same technology the labs use on the bench, providing a pre-extracted quantitative sampling event representing up to a hundred liters of water.

The small, dry extraction disk is all that is sent to the laboratory for solvent elution and analysis. This saves the costs of extraction, expensive cooler shipments of sample bottles, and seven day holding time requirements.

C.L.A.M.'s weigh just over one pound, including the four (4) AA batteries, and many can be easily taken to remote areas and left unattended to sample for days or weeks at submerged depths up to 100 feet.

We have simply taken the lab to the field and left the water behind

Unique Features

C.L.A.M.

Continuous Low-Level Aquatic Monitoring

Allows water to pass through SPE media first with its submersible design.

Special extraction disks are field hardened and remain outside the unit for easy replacement.

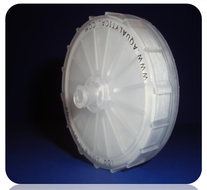
Low flow rates of 5-70 ml/min helps prevent premature plugging from floatables, as compared to high suction devices.

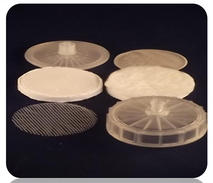
Disks can contain a variety of media to integrate non-polar and polar trace organics or even metals and nutrients.

Ability to integrate pollutants in 100 liters of water quantitatively, allowing ultra-low detection levels.

C.L.A.M.'s weigh just over one pound, including (4) AA batteries, and many can be easily taken to remote areas and left unattended to sample for days or weeks at submerged depths up to 100 feet.

Disk Design and Media Selection





The ***C.L.A.M.*** uses a variety of SPE media, dependent of the type of contaminate one is targeting. Our Gulf study utilized. the **Oasis® HLB** which is made from a specific ratio of two monomers, hydrophilic N-vinylpyrrolidone and lipophilic divinylbenzene (Waters, 2009). All the media types are housed in our custom housings which incorporate triple lofted glass pre-filters and supporting filters and inert screens to field harden and reduce clogging.

The Sampling Event-Dauphin Island

Dauphin Island is approximately 105 miles from the Horizon Spill Event. The oil released from Horizon was chemically dispersed, burned, emulsified and metabolized by wave action and indigenous bacteria . The sampling site at Dauphin Island had an influx of tar balls and emulsified oil mousse, which were analyzed for biomarkers and profiled by others, but it was our intent to study the effects of the oil release on the water column.

In order to do so, it was imperative to have a continuous unbroken extraction sampling event for a three month period, as we were monitoring a constantly changing and dynamic marine environment. It was also essential to obtain ultra-trace levels of detection only afforded by the C.L.A.M extraction system, since the oil was highly diluted and broken down by manmade and natural causation.

Sample Generation

The Water column was sampled at depths between 2-4 feet dependent on the tides, and excluded any surface inclusion. Each Disk was pre-spiked with 10 ug of Terphenly d-14 as a recovery field surrogate.The start and finish pumping volumes were recorded along with the time deployed.

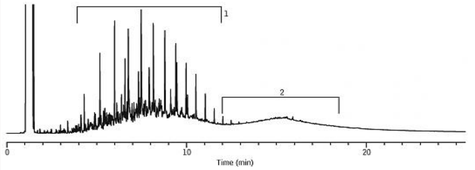
The total volume in liters extracted was calculated from this information, and was recorded on the chain of custody for the analytical quantitation. Results were reported in PPB for TPH and PPT for the PAH's due to the large volume of water that was extracted, which is an order of magnitude lower than a standard 1 liter grab sample.

Laboratory extraction and Analysis

Solvent elution of the field extracted disk follows EPA method 3550 for SPE elution procedures, it simply has to be solvent eluted and concentrated to a set extract volume. The extract solvent selection is instrument dependent. Our analysis required the use of GC/FID and GC/MS/MS so acetone and DCM were the elution solvents. The elution of the disks are performed in standard vacuum manifolds or with a simple syringe forcing or drawing solvent through the SPE media.

Total and dissolved organics were determined using a two stage filter system. The top disk is a depth filter which removes and collects pelagic sediments and oil droplets. The bottom SPE disk sequesters the dissolved trace organics.

Analytical Evaluations



Findings for TPH per EPA Method 8015

Analysis of the TPH as (C8-C24 and C24-C40) was performed using the standard GC/FID detection for fuel oil analysis. Because this method is analyzing a multi-component peak area of many thousands of individual co-eluting aliphatic and aromatic analytes, very low detection is not obtainable even extracting 50 liters or more of the Gulf sea water. Normal reporting limits for a 1 liter sample is normally 5 mg/l, the **C.L.A.M** extraction was analyzing down to 5 ug/l by extracting 50 liters, and found only a few hits that were just above the PQL as shown below:

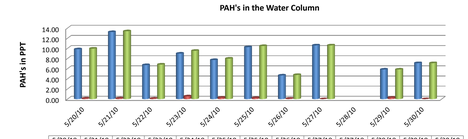
DATE	5-27-10	5-29-10	5-29-10	5-30-10	6-03-10	6-06-10	6-07-10	PQL
C8-C24 TPH	ND	13.10*	7.72*	ND	ND	6.57	ND	5 ppb
C24-C40 TPH	ND	20.70*	11.40*	ND	ND	10.5	ND	10 ppb

We found that using GC/MS/MS with 50 liter **C.L.A.M** extract the individual PAH components of the crude oil could be determined as a single peak analyte with great sensitivity in the sub part per trillion range. Since biomarker analysis of the crude oil would reveal the relative percent concentration of each PAH in the total crude oil, the total amount of the crude could be calculated with a degree of confidence.

Continuous Three Month PAH Gulf Study

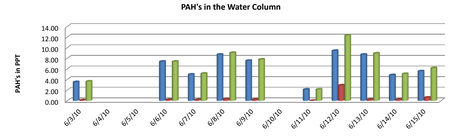
The PAH analysis were run using GC/MS/MS with D-14 Terphenyl as a field surrogate. Surrogates recoveries showed acceptable recoveries of 30%-110%.

May



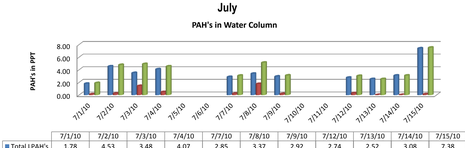
	5/20/10	5/21/10	5/22/10	5/23/10	5/24/10	5/25/10	5/25/10	5/26/10	5/27/10	5/27/10	5/29/10	5/29/10	5/30/10
Total LPAH's	9.83	13.22	6.71	8.98	7.71	10.24	7.07	4.67	10.60	3.22	5.25	5.84	7.10
Total CPAH,s	0.13	0.16	0.11	0.55	0.28	0.23	0.13	0.10	0.00	0.00	0.28	0.00	0.00
Total PAH's	9.96	13.38	6.82	9.53	7.99	10.47	7.20	4.77	10.60	3.22	5.53	5.84	7.10

June



	6/3/10	6/6/10	6/6/10	6/7/10	6/8/10	6/8/10	6/9/10	6/11/10	6/12/10	6/13/10	6/14/10	6/15/10
Total LPAH's	3.52	3.46	7.38	4.94	7.33	8.70	7.54	2.13	9.42	8.70	4.83	5.56
Total CPAH,s	0.11	0.19	0.00	0.18	0.15	0.33	0.23	0.00	2.90	0.22	0.23	0.60
Total PAH's	3.63	3.65	7.38	5.12	7.48	9.03	7.77	2.13	12.32	8.92	5.06	6.16

July



	7/1/10	7/2/10	7/3/10	7/4/10	7/7/10	7/8/10	7/9/10	7/12/10	7/13/10	7/14/10	7/15/10
Total LPAH's	1.78	4.53	3.48	4.07	2.85	3.37	2.92	2.74	2.52	3.08	7.38
Total CPAH,s	0.11	0.23	1.42	0.46	0.21	1.75	0.17	0.28	0.00	0.00	0.12
Total PAH's	1.89	4.76	4.90	4.53	3.06	5.12	3.09	3.02	2.52	3.08	7.50

We feel that this technology could monitor other oil rigs allowing them an unbroken record of the water column quality at or near their site, establish confidence of the water quality in the fishing and shell fish areas, and provide a novel tool to evaluate our oceans and streams for both total and dissolved trace organics...

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