

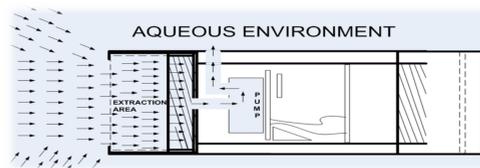
Time Integrative Dynamic Extractive Sampling



Trace organics in the water column are often extremely low. In the past, estimation of concentrations in the water column were obtained from indicator organism tissue residue studies, or passive samplers using equilibrium partitioning calculations, and complicated equations. The results were time integrative, but often qualitative as the results were dependent on temperature, bio-fouling, water flow, partition coefficients and motility. Only dissolved trace organic data could be obtained, values on particulate droplet, or pelagic contaminate laden sediments in water was not obtainable. In order to obtain both a dissolved and suspended fraction of the water column that provides both time integrative and quantitative data, a new dynamic research device was required.

The Device and Method

A Submersible SPE Extractive Sampler was Designed to meet these Requirements



The C.L.A.M. (Continuous Low-Level Aquatic Monitoring) was developed to produce this unique extract. The C.L.A.M. is a small submersible extraction sampler, using EPA approved methodology 3535, utilizing SPE (Solid Phase Extraction) media disks to sequester Pesticides, Herbicides, PAH's, TPH, and other trace organics from water.

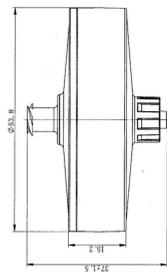


The C.L.A.M. actually extracts the water in-situ, with the same technology the labs use on the bench. It provides a pre-extracted quantitative sampling event, representing up to a hundred liters of water, lowering the laboratory detection limits a hundred fold. The small dry extraction disk is all that is sent to the laboratory for solvent elution and analysis.



C.L.A.M.s weigh just over one pound, including the 4 AA batteries, and many can be easily taken to remote areas and left unattended to sample continuously for up to 36 hours at submerged depths up to 100 feet in marine or fresh waters.

Media Disks Design and Capabilities



The C.L.A.M. uses field hardened disks to actively draw a known volume of water through the SPE media during the extraction event. All the SPE media types are supported in custom housings which incorporate inlet flow dispersion, triple lofted glass pre-filters, supporting filters, and inert screens to field harden and reduce clogging.



All the Media disks are designed with Luer Lok ends which can connect one or many disks together. Luer plugs are used to seal the disks before and after deployment, and for secure transport.



Media Disks can be "chained" for total/dissolved studies or to study any potential breakthrough.

- **C-18** - for neutral pesticides, and neutral 8270 compounds
- **DVB** - used as the C-18 media but will sequester compounds with greater polarity
- **HLB** - both Medium and Heavy polymer, is a solid-phase sample preparation product for the analysis of EPA Method 8270 (semi-volatile organics), EPA Method 1694 (pharmaceuticals and personal care products), endocrine disruptors, and other emerging contaminants in wastewater and drinking water.
- **8270 One Pass Disk** - this Disk incorporates HLB, Cationic and Anionic phases to extract neutrals, acids and bases from the water. The mixed medias provide an extremely wide array of polar and non-polar analytes.
- **Activated Carbon Disk** - sequesters very polar and or volatile organics, often run in extraction trains, where the disks can be Luer Locked together in any arrangement.
- **Pre-filter Disks** - developed for obtaining both total and dissolved trace organic fractions. Used in field extractions submerged in situ or on the bench. The disks can be Luer locked together to form a 2,3, or 4 disk extraction train, sequestering totals, dissolved, non-polars, and polars or breakthrough.
- **Specialty Media Disks** - new and evolving media types such as molecular imprinted polymers, carbon nano-tubes and various mixed media can be developed into a disk and housing assembly for selected research projects upon request.

Kow Values effect on Total and Dissolved Results

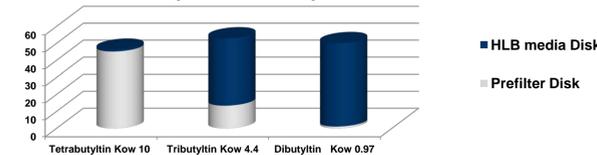
Organic micro contaminants have a wide array of polarities, and are given relative Octanol/ water Kow values. The Kow value determines the hydrophilic or phobic nature of the analyte. A simple lab study was conducted to show that water soluble analytes or polars were retained by the HLB media, and non-polars were retained on the glass pre-filter proportional to the KOW value.



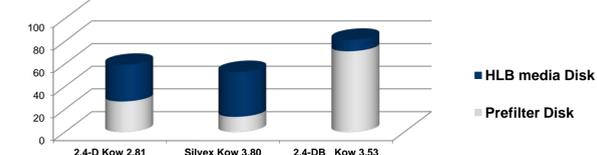
Total and dissolved organics were determined using a two stage Luer-Lok filter disk system. The first disk is a 1.5 micron depth filter disk, which removes and collects suspended trace organics, sediments and oil droplets. The second a HLB media disk which sequesters the dissolved trace organics and water oil emulsions.

Three sets of pre-filter and HLB media disks were spiked with Butylin chlorides, Phenoxy herbicides, and PAH's respectively. The disks then extracted 20 liters of pH neutral DI water. The pre-filter was separated from its media disk pair and both eluted individually with methanol and DCM. The extracts for Herbicides were converted to their methyl ester's and the Butylin converted to hexyl derivatives. The extracts were then concentrated to a 10 ml final volume. The results are shown below and display the recovery of each analyte on the pre-filter, the HLB media, and the kow value of each selected analyte analyzed.

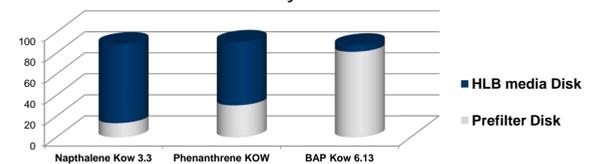
Butyltins % Recovery



Herbicides % Recovery



PAH % Recovery



The ability to extract for both dissolved and suspended micro contaminants in a time integrative, quantitative manner offers a new dimension in monitoring the dynamic marine and freshwater environment.

The Deep Water Horizon 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. The C.L.A.M., using submersible continuous extraction, was used to establish these ultra trace levels of oil and toxic components in the water column. This allowed 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.

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 bacteria. The sampling site at Dauphin Island had an influx of wave action, indigenous tar balls and emulsified oil mousse. These 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.



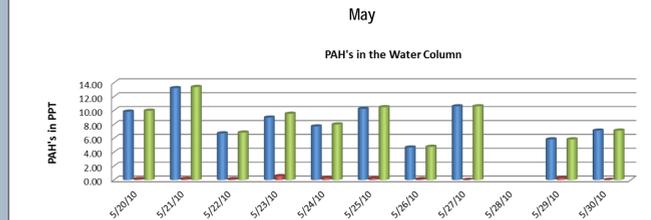
The Water column was sampled at depths between 2-4 feet dependent on the tides, and excluded any surface inclusion. Each Disk was pre-spiked with 10 ug of Terphenyl d-14 as a recovery field surrogate. The start and finish pumping volumes were recorded along with the time deployed.



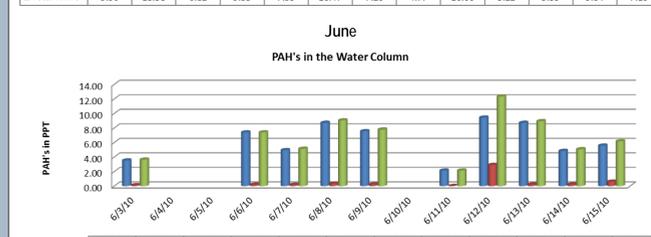
Solvent elution of the field extracted disk follows EPA method 3535 for SPE elution procedures, it simply has to be solvent eluted and concentrated to a set extract volume. The extract solvent selection is instrument dependent. Our analysis required the use of GC/FID and GC/MS/MS so acetone and DCM were 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.

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%.



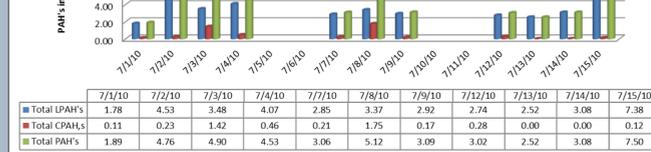
Date	Total LPAH's	Total CPAH's	Total PAH's
5/20/10	9.83	0.13	9.96
5/21/10	13.22	0.16	13.38
5/22/10	6.71	0.11	6.82
5/23/10	8.98	0.55	9.53
5/24/10	7.71	0.28	7.99
5/25/10	10.24	0.23	10.47
5/25/10	7.07	0.13	7.20
5/26/10	4.67	0.10	4.77
5/27/10	10.60	0.00	10.60
5/27/10	3.22	0.00	3.22
5/29/10	5.25	0.28	5.53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



Date	Total LPAH's	Total CPAH's	Total PAH's
6/3/10	3.52	0.11	3.63
6/6/10	3.46	0.19	3.65
6/6/10	7.38	0.00	7.38
6/7/10	4.94	0.18	5.12
6/8/10	7.33	0.15	7.48
6/8/10	8.70	0.33	9.03
6/9/10	7.54	0.23	7.77
6/11/10	2.13	0.00	2.13
6/12/10	9.42	2.90	12.32
6/13/10	8.70	0.22	8.92
6/14/10	6.16	0.23	6.39
6/15/10	5.56	0.60	6.16



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



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

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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