Time Integrative Large Volume In Situ Water Extraction Total and Dissolved Trace Organics.

AQUALYTICAL

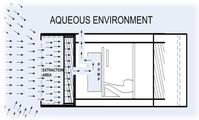
C·I·Agent STORM·WATER SOLUTIONS

The Ultra Low Requirement

In the summer of 2011, C.I. Agent Storm•Water Solutions coordinated with the City of Los Angeles Watershed Protection Division and Environmental Monitoring Division to study **ultra** low level contamination of Organochlorine Pesticides at the end of Ballona Creek just before it enters the Pacific Ocean. They wanted the study to provide a continuous, time integrative and quantitative data within a 24 hour window. It was also important for them to utilize their Laboratory for the extraction and analysis.

The Device and Method

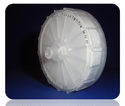
The **C.L.A.M.** (Continuous Low -Level Aquatic Monitoring) was developed to meet this requirment. The **C.L.A.M.** is a small submersible extraction sampler, using EPA approved methodology 3535, utilizing SPE (Solid Phase Extraction) media to sequester Pesticides, Herbicides, PAH's, TPH, and other trace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



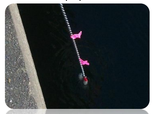
. **C.L.A.M.**s weigh just over one pound, including the 4 AA batteries, and many can be easily taken to remote areas and left unattended to sample continuously for up to 36 hours at submerged depths up to 100 feet in marine or fresh waters.

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

Sampling and Media Selection



The ***C.L.A.M.*** uses a variety of SPE media, dependent of the type of contaminate one is targeting The L.A 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 custom housings which incorporate triple lofted glass pre-filters and supporting filters and inert screens to field harden and reduce clogging.

The CLAMs were spiked with PRC's, calibrated for flow, and deployed pumping submerged for 29 hours. The watershed personnel arrived the next day to take their grab samples. The CLAMs were raised back on to the bridge with the stainless steel chain, and the same calibration procedure was performed to determine final flow rate. The total volume of water processed through the HLB media could now be calculated to give a quantitative concentration of the analytes targeted

Analytical recovery of Target Analytes and PCR's

The results from all of the1 liter grab samples the LA City laboratory ran for Ballona Creek, were non-detect >0.01 ug/l, for the 8081 target pesticides. The C.L.A.M 24 hr large volume sampling event yielded the legacy DDT metabolite 's DDE and DDD, the BHC's , Dieldrin and Endosulfan.

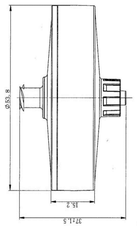
The ability to obtain a whole water sample extract, yielding sub ppt values, in a continuous 24 hour extraction event, can allow the environmental community the ability to keep up with the decreasing concentrations of pesticides on the 303(d) lists, as well as determine TMDLs without overestimations from high levels of non-detects.

	RL, ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
A-BHC	0.0001	0.0001	0.0001	0.0001	0.0001	nd<0.01
G-BHC	0.0001	0.00008	nd	0.00004	0.00003	nd<0. 01
Heptachlor	0.0001	nd	0.00004	nd	nd	nd<0.01
Aldrin	0.0001	nd	0.00004	nd	nd	nd<0.01
B-BHC	0.0001	nd	0.00013	0.00009	0.00009	nd<0.01
D-BHC	0.0001	nd	0.00006	nd	nd	nd<0.01
Heptachlor Epoxide	0.0001	nd	0.00006	nd	nd	nd<0.01
2,4'-DDE	0.0001	0.00006	0.00006	nd	nd	nd<0.01
Endosulfan I	0.0001	nd	0.00009	0.00004	0.00006	nd<0.01
4,4'-DDE	0.0001	nd	0. 00014	nd	nd	nd<0.01
Dieldrin	0.0001	0.00009	0.00013	0.00005	0.00007	nd<0.01
2,4'-DDD	0.0001	nd	nd	nd	nd	nd<0.01
Endrin	0.0001	nd	nd	nd	nd	nd<0.01
2,4'-DDT	0.0001	nd	nd	nd	nd	nd<0.01
4,4'-DDD	0.0001	0.00008	0.00013	0.00005	nd	nd<0.01
Endosulfan II	0.0001	nd	nd	nd	nd	nd<0.01
4,4'-DDT	0.0001	nd	nd	nd	nd	nd<0.01
Endrin Aldehyde	0.0001	nd	nd	nd	nd	nd<0.01
Mirex	0.0001	nd	nd	nd	nd	nd<0.01
Endosulfan II Sulfate	0.0001	nd	nd	nd	nd	nd<0.01
Methoxychlor	0.0001	nd	nd	nd	nd	nd<0.01
TCMX-SURR #1	0.0001	10%	23%	32%	50%	
DBC-SURR #2	0.0001	19%	28%	41%	62%	
Sample volume, Liters		89.4L	69.7L	79.2L	70.2L	1.0L
Sampling Date		7/12/11	7/12/11	8/23/11	8/23/11	7/12/11-8/23/11
Preparation date		7/25/11	7/25/11	9/2/11	9/2/11	7/25/11-9/2/11
Values are based on 10ml extract		Disk 1	Disk2	Disk 3	Disk 4	

nd=not detected, NA=not analyzed

Quality Control met EPA and Laboratory Acceptance Criteria

Below are the values obtained using the HLB disk as a laboratory control spike during the preparation dates . The lab personnel had not used SPE extraction before and changes in the solvent elution volume and technique made a vast improvement in the PRC recoveries. The field surrogate recoveries, and the LCS recoveries for the 7/25/2011 preparation date failed the labs in house criteria for surrogate and LCS recovery data, but passed EPA method criteria. The disks prepared 09/01/2011 passed both field surrogate and LCS recovery criteria for both EPA and laboratory. The disks also produced a clean ND blank extract which is critical for low level detection analysis.



Target Analytes	7/25/11 Recovery %	0/25/11 Recovery %	Lab Criteria	EPA Criteria
A-BHC	49	73	84-114	37-134
G-BHC	48	72	82-112	32-127
Heptachlor	45	87	67-103	34-111
Aldrin	67	88	71-103	42-122
B-BHC	49	63	83-113	17-147
D-BHC	37	67	75-116	19-140
Heptachlor Epoxide	73	84	80-113	37-142
2,4'-DDE	NA	NA	85-115	
Endosulfan I	70	85	77-114	45-153
4,4'-DDE	69	90	75-131	30-145
Dieldrin	76	88	75-114	36-146
2,4'-DDD	NA	NA	87-120	
Endrin	83	94	66-126	30-147
2,4'-DDT	NA	NA	78-122	
4,4'-DDD	81	90	77-113	31-141
Endosulfan II	67	80	78-112	D-202
4,4'-DDT	83	94	75-113	25-160
Endrin Aldehyde	29	62	50-107	
Mirex	NA	NA	85-115	
Endosulfan II Sulfate	64	73	57-131	26-144
Methoxychlor	94	94	74-120	
TCMX-SURR #1	27	52	33-128	
DBC-SURR #2	42	59	40-143	
Sample volume, Liters	1	1		
Values are based on 10ml extract				

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?

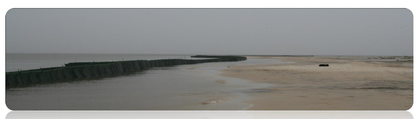
Crude oil and component PAH concentrations in the marine water column are extremely low, even after a spill event. In the past, estimations of PAH concentrations in the water column were obtained from mussel and fish tissue residue studies, using equilibrium partitioning calculations.

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 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.

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.

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.

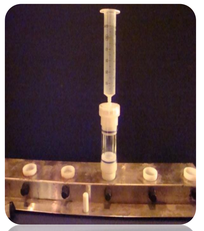


Sample Generation

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 Terphenyl 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 PPT for the PAH's due to the large volume of water usually (60-80 liters), that was extracted. The enhanced extraction volumes allowed almost two orders of magnitude lower detection, than a standard 1 liter grab sample.

Laboratory extraction and Analysis

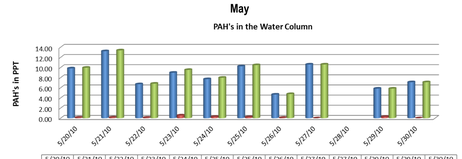


Solvent elution of the field extracted disk follows EPA method 3535 for SPE elution procedures, it simply has to be solvent eluted and concentrated to a set extract volume. The extract solvent selection is instrument dependent. Our analysis required the use of GC/FID and GC/MS/MS so acetone and DCM were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

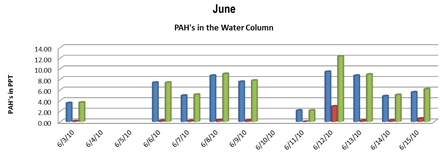
Total and dissolved organics were determined using a two stage filter system. The top disk is a depth filter which removes and collects pelagic sediments and oil droplets. The bottom SPE disk sequesters the dissolved trace organics. The analysis for TPH was performed using flame ionization, which yielded no hits above the RL, because of the multi-component peaks and the low sensitivity of the FID, the Ion-Trap GC/MS/MS. Was used to monitor the single peak bio-markers and the PAH's in the PPT range.

Continuous Three Month PAH Gulf Study

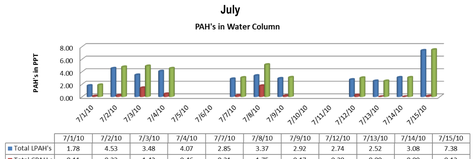
The PAH analysis were run using GC/MS/MS with D-14 Terphenyl as a field surrogate. Surrogates recoveries showed acceptable recoveries of 30%-110%.



	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 CPAHs	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



	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 CPAHs	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



	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 CPAHs	0.11	0.23	1.42	0.46	0.21	1.75	0.17	0.28	0.00	0.00	0.32
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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