AQUALYTICAL

The Problem with Water Sampling

Standard grab sampling only provides a few second snap shot in time, of a changing dynamic system

Automatic samplers are bulky, heavy, and expensive. Hydrophilic contaminates will adhere to the bulk container walls and tubing, biasing the results low. They only provide a liter aliquot, an intermittent sample, and standard reporting limits. **Passive samplers** provide a long term integrative partitioning event, but are effected by temperature, flow and bio-fouling and are dependent on complicated mathematical modeling for any quantitative values.

"The *ideal* continuous sampler should be small, stealth, and able to continuously field sample for extended periods of time providing a time integrative quantitative extract. It should also be immune to the effects of temperature, flow and bio-fouling, and provide ultra-low quantitative detection capabilities if necessary."

The Solution

A submersible SPE extractive sampler was developed to provide this ideal sample

AQUEOUS ENVIRONMENT	

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 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 50 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 preextracted 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.





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



Solid Phase HLB Extraction Disks The disk will retain the widest range of nonpolar and polar compounds, and is the standard disk of choice for new emerging contaminates of concern such as pharmaceuticals, personal care products, steroids and herbicides.

Solid Phase C-18 Extraction Disks

This Disk has been in use for many years and many methods have incorporated its use. It is quite diverse and may be used for the standard EPA1664 gravimetric Oil & Grease determination if it is eluted with Hexane, or analyzed for TPH by EPA Method 8015, PAH's, PCP's, PCB's, Dioxins, Furans, PBDE's.

Lofted Glass Pre-Filtration Disks

This filter assembly uses the triple lofted glass fiber filters to remove suspended sediment from the water. It allows for toxological studies for total and dissolved trace organics, when used in a two stage filter assembly, where the filtration disk removes the sediment and allows the water soluble organics to be retained on the bottom HLB or C-18 media disk.

Specialty Media: Other medias provided by Atlantic[™] disk can be incorporated into our disk housings. Mixed medias and specialized loadings can be arranged with a 50 disk manufacture minimum order. Some of these include:

- •Atlantic[™] 8270 One Pass Disk
- •Atlantic[™] DVB Disk

Continuous Low-Level Aquatic Monitoring

The C.L.A.M.

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.

Luer Lok ends which can connect one



The SPE media disks encased in the C.L.A.M. disks are the same used by laboratories for the SPE 3535 extractions world wide. A large media selection is available as shown in the samples below:

Media Selection



•Specialty media loading amounts of the above media selections

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 dried with methanol, eluted with the appropriate solvent, and concentrated to a set extract volume. The extract solvent selection is instrument dependent.





The elution of the disks is performed in standard vacuum manifolds, or with a simple syringe forcing or drawing solvent through the SPE media into a separatory funnel where the solvent is partitioned with pH 2 water to remove the methanol from the elution solvent

The Deep Water Horizon Continuous Extraction 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?

The C.L.A.M., using submersible continuous extraction, was able to establish these ultra trace levels of oil and toxic components in the water column off Dauphin Island, AL. The C.L.A.M. provided an unbroken daily extractive event for three months allowing daily tracking of PAH's in the water column.

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. PAH's in the Water Column





C.L.A.M. - Enhancing University Research

The C.L.A.M has given university researchers a powerful new tool which enhances not only detection but extraction and storage of a large volume time integrative event.

Research Projects



Duke Effect Directed Analysis on three wastewater impacted golf course storm water retention ponds. Field Toxological and Chemical studies using C.L.A.M. time integrative extractive storage.



Nebraska



Research for long term effects of Deep Water Horizon Spill PAH analysis in marshes of Mississippi Delta Deep water near well being processed through disks PAH stratification through water column published in 2014



Group (Algalita/5 Gyres Institute) that has studied other ocean Gyres. In South Atlantic in November, 2010, C.L.A.M Trolled 2-8 knots through open ocean. See Chelsea Rochman presentation – SETAC 2013



Results

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 Pesticides.



- One liter grab samples ND at >0.01 ug/l for pesticides
- CLAM 24 hr Extraction Yielded legacy DDE, DDD, Dieldrin, BHC's, and Endosulfan in PPT
- Laboratory QA/QC improved, and met EPA and house acceptance criteria for all analytes.
- Extraction and Analysis was performed in house using established laboratory procedures.

•. 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	7/12/11-8/2
Preparation date		7/25/11	7/25/11	9/2/11	9/2/11	7/25/11-9/
Values are based on 10ml extract		Disk 1	Disk2	Disk 3	Disk 4	
nd=not detected, NA=no	t analyzed					



USGS Comparison and Validation

15 mi downstream

Benzophenone Bromoform Camphor Ethyl citrate

*≊***USGS**

Water samples collected using the C.L.A.M. were compared to those collected using polar organic chemical integrative samplers, POCIS, and using standard discrete grab methods. For all three sampling methods, lab analysis for organic waste-indicator compounds was performed by the U.S. Geological Survey's National Water Quality Laboratory (NWQL).





9 COMPOUNDS WERE DETECTED BY CLAM METHODS ONLY

4 COMPOUNDS WERE DETECTED BY CLAM AND DISCRETE SAMPLE METHODS

0 COMPOUNDS WERE DETECTED BY THE DISCRETE WATER SAMPLE METHOD ONLY



Wastewater Dominated River – at outfall and

3 COMPOUNDS WERE DETECTED

BY ALL 3 SAMPLING METHODS

Other Projects

ECOLOGY State of Washington

Washington State Dept. of Ecology – Spokane River - ultra trace levels of PCB congeners, Aroclors, PBDE's and Dioxins

- See Poster Session for Data SETAC 2013
- GeoEngineers performing more Spokane River deployments 10/13
- Washington DOE performing more deployments 11/13



California Fish & Wildlife has contracted with California Central Valley Regional Water Board and CA Dept. of Pesticide Regulation to analyze CLAM disks •Current work on Battle Creek for pesticides



California Regional Bight Monitoring – 54 C.L.A.M. Deployments recently completed for PCBs, PDBEs and pesticides - 2014 publications

Contact information

CI-Agent Storm-Water Solutions Research & Development Center Brent Hepner 23010 S.E 222nd St. • Maple Valley, WA 98038 T: 253-732-5319 E: b.hepner@aqualytical.com