Low Level Detections of Organochlorine Pesticides
Ballona Creek, Los Angeles, CA - Summer 2011

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 low level contamination of Organochlorine Pesticides at the end of Ballona Creek just before it enters the Pacific Ocean. The Aqualytical division of C.I. Agent Storm•Water Solutions has developed a device called the **C.L.A.M.** (Continuous Low -Level Aquatic Monitoring). The **C.L.A.M.** is a small submersible extraction sampler, using EPA approved methodology, utilizing SPE (Solid Phase Extraction) media 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.

The use of this unique technology provides the ultra low detection necessary to find and quantitate the low levels of trace organics in the water column. Before, the laboratory could only analyze a single liter of water representing only a few seconds snapshot in time. The **C.L.A.M.** will provide ultra low detection, continuous coverage of hours to days, and cost savings, as the small pre-extracted disk is all that is sent to the laboratory for a simple elution prior to analysis. **We simply have taken the laboratory to the field, and left the water behind.**

Preparation for Sampling

After discussions with the Watershed Protection Division and the Environmental Monitoring Division of the City of Los Angeles, a need was identified to investigate low level contamination of Organochlorine Pesticides per EPA Method 8081, near the end of Ballona Creek at the location shown below:

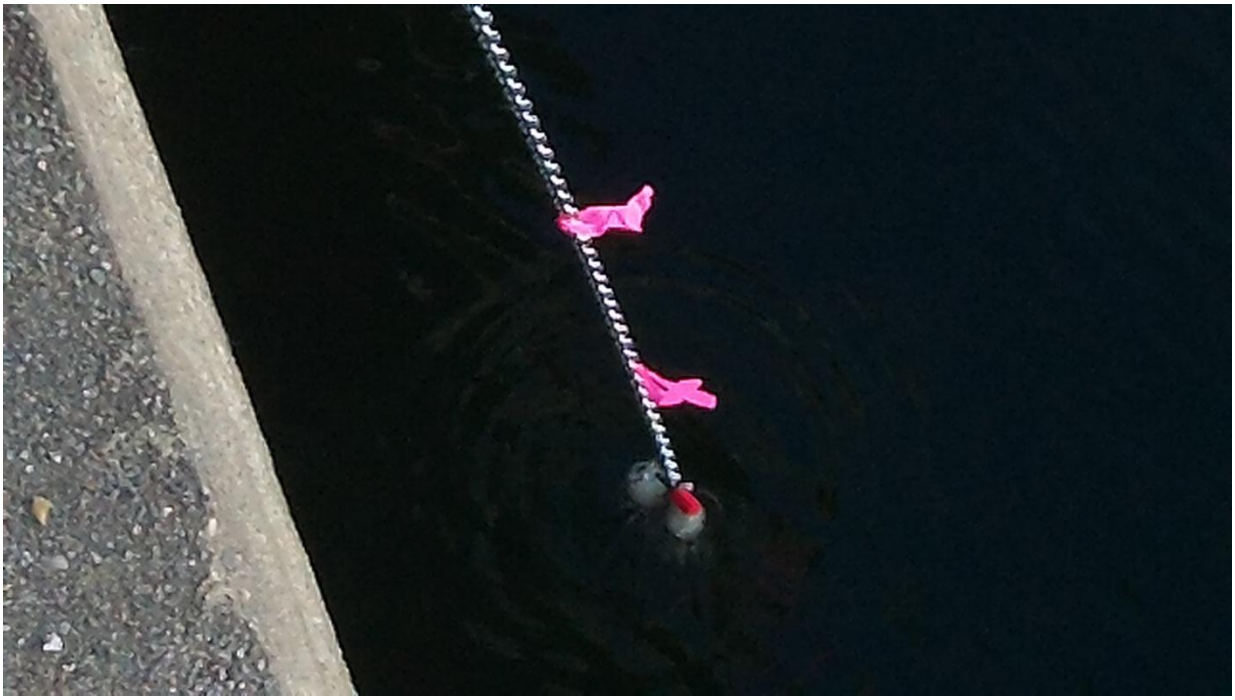
HLB Media was chosen for this analysis as it could sequester a wider range of polar and non-polar target analytes than most any other specific polarity range media. Seven new, unconditioned HLB Disks were sent to the lab at the Environmental Monitoring Division in Los Angeles. The chemist there conditioned the disks following the EPA method 3535 for Organochlorine Pesticides as follows: The disk was first washed with DCM, the eluting solvent, to remove any trace of contaminates in the new disk. The DCM was vacuumed to dryness, and Methanol was added to the disk and allowed to soak for a minute. The last step involved drawing off the Methanol under vacuum and displacing it with distilled water. The 8081 Surrogates of TCMX and DCB were then spiked into the disk followed by an additional 50 ml of distilled water being drawn through . The disks were then sealed with the Luer-Lock plugs provided, and refrigerated until needed for deployment. The HLB media is a self wetting lipophilic-lipophobic polymer, so once conditioned, it can be stored for many months, unlike other silica-gel based medias.

Sampling Event

It was determined that the Watershed Protection Division would be taking their monthly grab samples at Ballona Creek on July 12, 2011. The location for this sampling is the water under the middle of the bridge at Pacific Ave. where it crosses Ballona Creek per the previous map. An arrangement was made with Watershed personnel to meet at the bridge at 7am on July 11, 2011. The retrieval would then occur alongside the grab sampling the following day to get an extraction event longer than 24 hours.

On July 11, two CLAMs were assembled and outfitted with HLB Extraction Disks to provide a duplicate for the low level analysis. The CLAMs were calibrated for initial flow rate in a rinsed bucket of water obtained next to the bridge. Both CLAMs were tie wrapped and locked to a stainless steel chain, and once the initial flow rates were determined through calibration, they were lowered off the deck of the bridge and put about 3 feet underwater to ensure they would stay submerged even in low tide, as this location is close enough to the ocean to be subject to tidal influence. The CLAMs were left in the water for approximately 29 hours until 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.

On August 22 and 23, the same progression was followed to obtain another set of duplicate CLAM data alongside Watershed grab sampling.



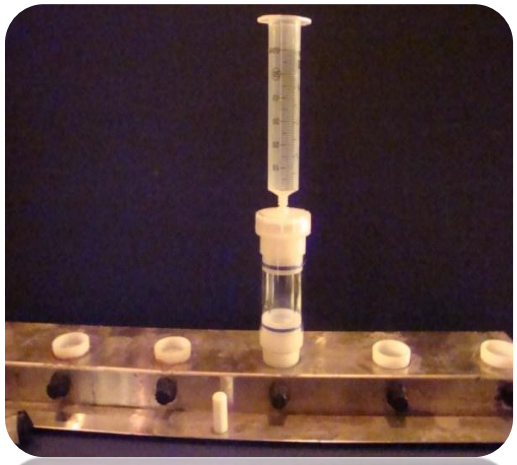
Laboratory Preparation

Once the Los Angeles Environmental Monitoring Division received the HLB Extraction Disks deployed in the field, the disks were eluted following EPA method 3535 in the following manner:

1. Vacuum dry the disk for 10 minutes to remove excess water retained in disks.
2. Add 50 ml of methanol, let soak for 2 minutes and vacuum and collect the elutant.
3. Add 50 ml of DCM to the disk, let soak again for 2 minutes, vacuum collect and combine with the methanolic elutant. Repeat step three again and combine the elutants.*
4. The eluted solvents are then washed with DCM into a 250 ml separatory funnel, 150 ml of distilled water is added . The funnel is then shaken for two minutes to remove the methanol from the DCM by partitioning. After settling the DCM is collected in a concentrative vessel, blown down, then exchanged to Hexane and concentrated to a 10 ml final volume.
5. The Extract is now ready for ECD analysis for method 8081 Organochlorine pesticides.

*(*The increased amounts of solvent used is due to the large pre- filter dead volume used in the C.L.A.M field SPE disk)*

Extraction Manifold



HLB Extraction Disk

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ANALYTICAL RESULTS

The extract from the C.L.A.M. large volume sampling was run in duplicate. Each analytical batch represented a field blank, sample results, matrix spike, and a comparison grab sample. The instrument data results from the City of Los Angeles Lab are included in the table below:

HLB Disk 10 ML Solvent Extract Concentration

Instrument: Varian#2
Analyst: Rizalina Hamblin

Sample received date:		7/12/11	7/12/11	8/23/11	8/23/11					
Sample preparation:		7/25/11	7/25/11	9/1/11	9/1/11	9/1/11	7/25/11	9/1/11		
analysis date:		8/18/11	8/18/11	9/2/11	9/2/11	9/2/11	8/18/11	9/2/11		
		Disk 1	Disk 2	Disk 4	Disk 5	Disk 3	Disk 7	Disk 6		
	RL, ug/L	BCE-1A ug/L	BCE-1A ug/L	BCE-1A ug/L	BCE-1A ug/L	Blank ug/L	LCS % Rec	LCS % Rec	Control Chart Limits (%)	EPA Limits (%)
A-BHC	1	0.9	0.7	0.8	0.8	nd	49	73	84-114	37-134
G-BHC	1	0.7	nd	0.3	0.2	nd	48	72	82-112	32-127
Heptachlor	1	nd	0.3	nd	nd	nd	45	87	67-103	34-111
Aldrin	1	nd	0.3	nd	nd	nd	67	88	71-103	42-122
B-BHC	1	nd	0.9	0.7	0.6	nd	49	63	83-113	17-147
D-BHC	1	nd	0.4	nd	nd	nd	37	67	75-116	19-140
Heptachlor Epoxide	1	nd	0.4	nd	nd	nd	73	84	80-113	37-142
2,4'-DDE	1	0.5	0.4	nd	nd	nd	NA	NA	85-115	
Endosulfan I	1	nd	0.6	0.3	0.4	nd	70	85	77-114	45-153
4,4'-DDE	1	nd	1	nd	nd	nd	69	90	75-131	30-145
Dieldrin	1	0.8	0.9	0.4	0.5	nd	76	86	75-114	36-146
2,4'-DDD	1	nd	nd	nd	nd	nd	NA	NA	87-120	
Endrin	1	nd	nd	nd	nd	nd	83	94	66-126	30-147
2,4'-DDT	1	nd	nd	nd	nd	nd	NA	NA	78-122	
4,4'-DDD	1	0.7	0.9	0.4	nd	nd	81	90	77-113	31-141
Endosulfan II	1	nd	nd	nd	nd	nd	67	80	78-112	D-202
4,4'-DDT	1	nd	nd	nd	nd	nd	83	94	75-113	25-160
Endrin Aldehyde	1	nd	nd	nd	nd	nd	29	62	50-107	
Mirex	1	nd	nd	nd	nd	nd	NA	NA	85-115	
Endosulfan II Sulfate	1	nd	nd	nd	nd	nd	64	73	57-131	26-144
Methoxychlor	1	nd	nd	nd	nd	nd	94	94	74-120	
TCMX-SURR #1	1	10%	23%	32%	50%	17%	27	52	33-128	
DBC-SURR #2	1	19%	28%	41%	62%	26%	42	59	40-143	
Sample volume, Liters		89.4L	69.7L	79.2L	70.2L					
Values are based on 10ml extract										

Spike std conc. in 10ml extract: Pesticides (30ppb), surrogates (40ppb)
nd=not detected, NA=not analysed

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Calculated Pesticide Results based on Water Volume Extracted

Sample received date:		7/12/11	7/12/11	8/23/11	8/23/11	
Sample preparation:		7/25/11	7/25/11	9/1/11	9/1/11	9/1/11
analysis date:		8/18/11	8/18/11	9/2/11	9/2/11	9/2/11
		Disk 1	Disk 2	Disk 4	Disk 5	Liter Grab
		BCE-1A	BCE-1A	BCE-1A	BCE-1A	
	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

Values are based on 10ml extract

Spike std conc. in 10ml extract: Pesticides (30ppb), surrogates (40ppb)
nd=not detected, NA=not analyzed

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Reporting Limit and Method Detection Limit

The RLs are based on 5 X the MDLs of 0.2 ug/l. The instrument area counts were 89.4 times higher in Disk #1 as compared to the 1liter grab sample, due to the amount of water they both extracted. This provided the magnification necessary to see pesticides that were not previously detected. Non-detect results do not indicate whether the contaminant is present at a concentration just below the detection limit or present at a concentration just above zero, or absent from the sample. Therefore, contaminants that were evaluated as non-detects can lead to an **overestimation** of risk if the actual concentrations are just above zero, or absent from the sample. It should be noted that the extract volume was 10 ml. Often laboratories will concentrate samples to 1ml to enhance their sensitivity. If this were the case the 89.4 liter extraction from disk #1 would supply a reporting limit of 0 .01 part per trillion and a MDL of 0.002 part per trillion or 2 parts per quadrillion!

Quality Assurance

The results reported with the enhanced extraction volumes were still at or below the RL, for this reason sporadic duplicate results were seen on the first set of extraction disks prepared on 7/25/2011, the results on the second set of disks prepared on 9/02/2011 were more consistent. This can be accounted for in the extraction technique improvement as shown in the surrogate percent recoveries for the two 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 surrogate recoveries in the field samples and the laboratory control spike recoveries for the analytical batches. 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.

Discussion

The results from all of the1 liter grab samples the LA City laboratory 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. These pesticides were found at or below the RL but above the MDL as estimated values. Simple concentration to a one ml extract would yield numbers all above the RL.

The ability to obtain a whole water sample extract, yielding sub ppt value, 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. It should be recognized that the C.L.A.M disks can be staged to include a depth filter prior to the SPE media disk, allowing total and dissolved studies done on a whole water sample in-situ. The Extracts from the C.L.A.M disk could be used on most any trace organic with a Kow value above 1.5, using the HLB media designed for CEC's and pharmaceuticals, or other specific medias for very polar targets of interest. The same extract can also be used in a bioassay directed analysis, using effect directed analysis (EDA) techniques. Today it is not necessary to have to wait months for passive results when same day active results are available.

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