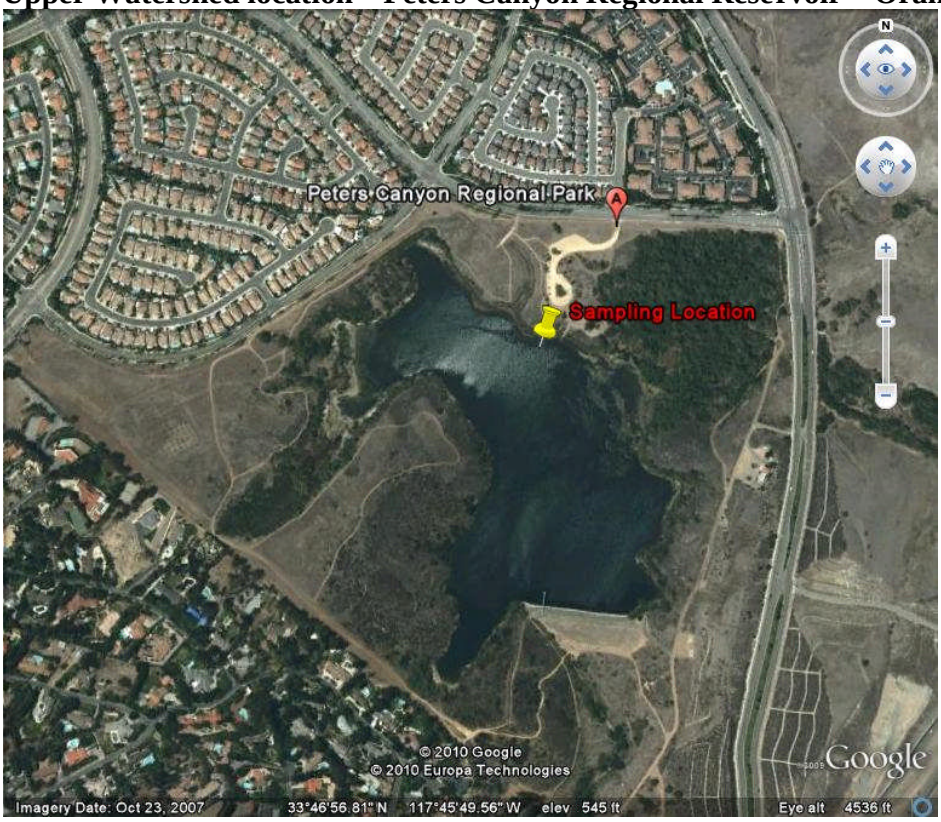
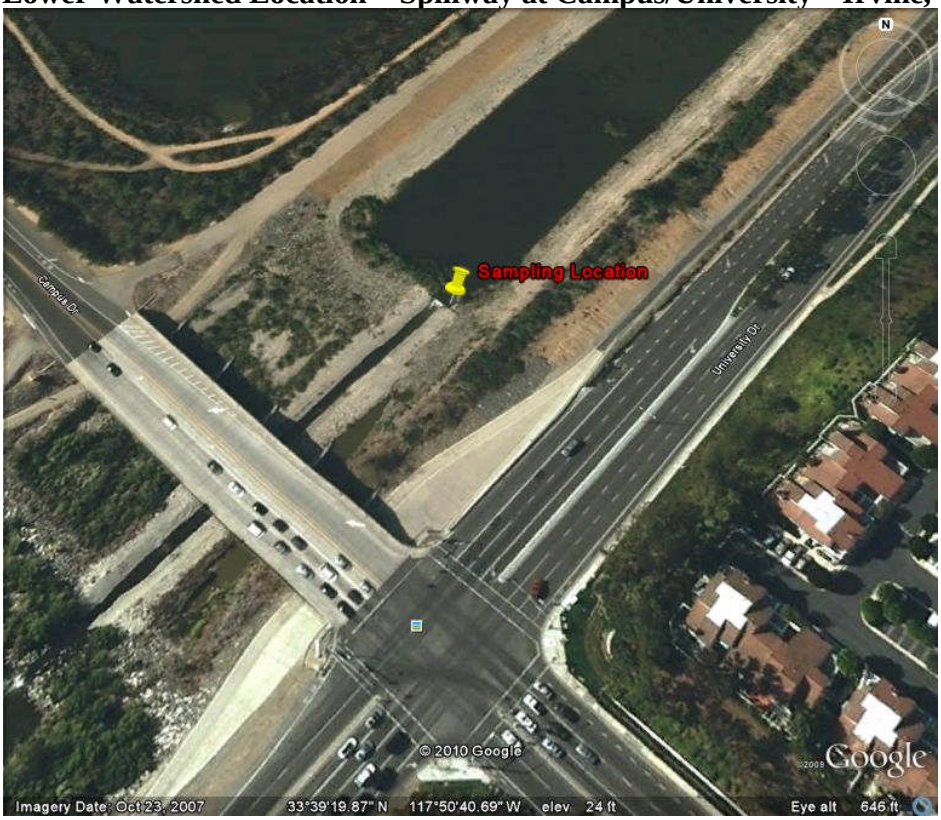
C.L.A.M. Field Evaluation
March/April 2010
Orange County, California
In Conjunction with the
Southern California Coastal Water Research Project

Upper Watershed location – Peters Canyon Regional Reservoir – Orange, CA



Lower Watershed Location – Spillway at Campus/University – Irvine, CA



Project Description

Aqualytical Services, Inc. coordinated with the Southern California Coastal Water Research Project (SCCWRP) to evaluate the presence of pesticides in an Orange County watershed in the spring of 2010. Aqualytical deployed the Continuous Low-level Aquatic Monitors or C.L.A.M.s at both the Campus Spillway and at Peters Canyon Reservoir alongside SCCRWP deployments of 3 different types of passive samplers, the POCIS, SPME, and PED.

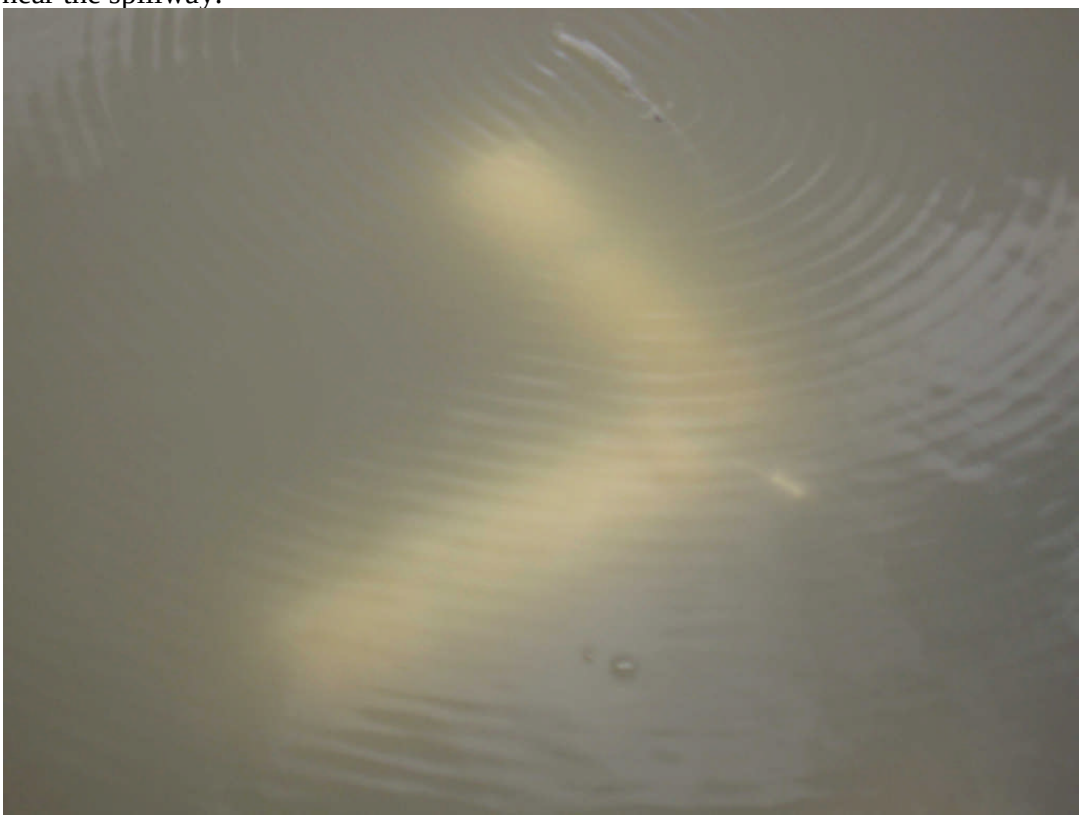
The C.L.A.M. is described in Appendix A.

SCCWRP has an interest in determining the levels of pesticides, specifically the class of pesticides called pyrethroids, in the San Diego Creek watershed that feeds Newport Bay in Orange County, California.(See Appendix B for a list of compounds targeted) The lower watershed is heavily urbanized. Just above the tidal/brackish influence of Newport Bay is a spillway in Irvine, CA at the intersection of Campus/University. This location was chosen as the lower watershed sampling point.

Near the top of the watershed lies Peters Canyon Regional Reservoir, whose drainage area includes some agricultural, some natural landscape, and a small amount of suburban development inputs.

On March 8, 2010, Aqualytical met SCCWRP at the Campus Spillway for the initial deployments. This date was chosen as it was the day after a significant rain event. SCCWRP had contracted Mactec to pull flow composite grab samples during the storm event as part of the sampling protocol.
Aqualytical deployed 2 C.L.A.M.s as shown in the following photos:

The C.L.A.M.s were attached to rods that were driven into the mucky, fine silt bottom near the spillway:



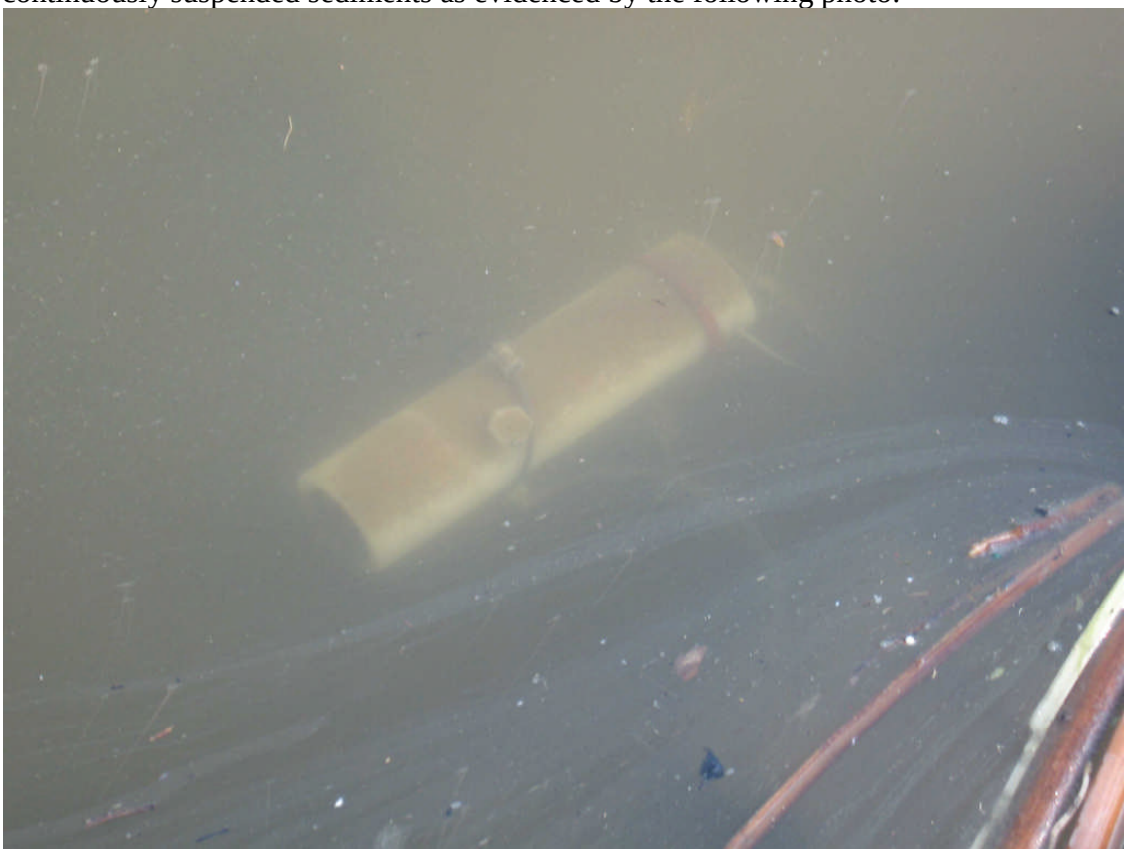
SCCWRP deployed the POCIS, SMPE, and PED as shown in the following photo:

SCCWRP stated that the deployment time for the passive samplers needed to be at least 18 days. They are looking for the passive samplers to come to an equilibrium with the analyte concentration in the water body.

The C.L.A.M. models used in this event extract 50-100 liters of water in a 24 hour period, giving 50-100 times the magnification of a 1 liter grab sample. At deployment, the C.L.A.M. is calibrated to determine the initial flow rate in ml/min. At the end of the deployment period the C.L.A.M. is calibrated again to determine the final flow rate in ml/min. In some cases an intermediate calibration was also performed. The flow rates are averaged and the total time is documented to provide a total water volume extracted for the sampling event.

See C.L.A.M. Deployment Instructions in Appendix C.

C.L.A.M.s were deployed daily for the following 11 days after initial deployment. The slow moving water just above the Campus Spillway was found to contain very fine continuously suspended sediments as evidenced by the following photo:



Because of the fine sediment, flow was restricted faster than anticipated and volumes analyzed were between 10-50 Liters.

On March 8 SCCWRP deployed the same passive sampler rig at Peters Canyon as deployed at the Campus Spillway. On March 19, C.L.A.M.s were deployed at the Peters Canyon Reservoir site a few feet away from the passive sampler deployment.

At Peters Canyon, there was not near the fine suspended sediment as at Campus Spillway. Over the following 14 days, volumes analyzed ranged between 30-80 Liters.

As rain was expected, SCCWRP pulled the passive samplers on March 30. The C.L.A.M.s were deployed until April 1 in hopes of capturing the rain event, but the rain event did not materialize.

Following are the analytical results from the C.L.A.M. deployments with a discussion of the results.

Results from the SCCWRP Passive Sampler deployments are not expected until July/August of 2010.

Appendix A

Continuous Low-Level Aquatic Monitoring

The **CLAM** is a submersible extraction sampler, using EPA approved SPE (Solid Phase Extraction) media to sequester Pesticides, Herbicides, PAH's, TPH, and other trace organics from water.

The device uses low flow rate extraction sampling (5-60 ml/minute), where water is drawn continuously through the extraction media. The **CLAM** provides an extraction event that can be hours, days or weeks long, allowing capture of trace pollutants from illicit and episodic events. Standard grab sampling only provides a few second snap shot in time, of a changing dynamic system, and a liter sample to take to the laboratory for extraction and analysis.

The **CLAM** 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 laboratories detection limits a hundred fold. 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. We have simply taken the lab to the field and left the water behind!

CLAM'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 for days or weeks at submerged depths up to 100 feet. They are applicable for sampling of; urban water systems, rivers, monitoring wells, drinking water systems, watersheds and lakes, agricultural runoff, storm water and marine environments.

Appendix B

List of Compounds Targeted (Pyrethroids)

Bifenthrin
Cypermethrin
Cyfluthrin
Deltamethrin
Cyhalothrin
Permethrin
Esfenvalerate
Fipronil
fipronil sulfon
fipronil desulfinyl
fipronil sulfide
Chlorpyrifos
Diazinon
Methoprene
Atrazine
simazine

Appendix B continued

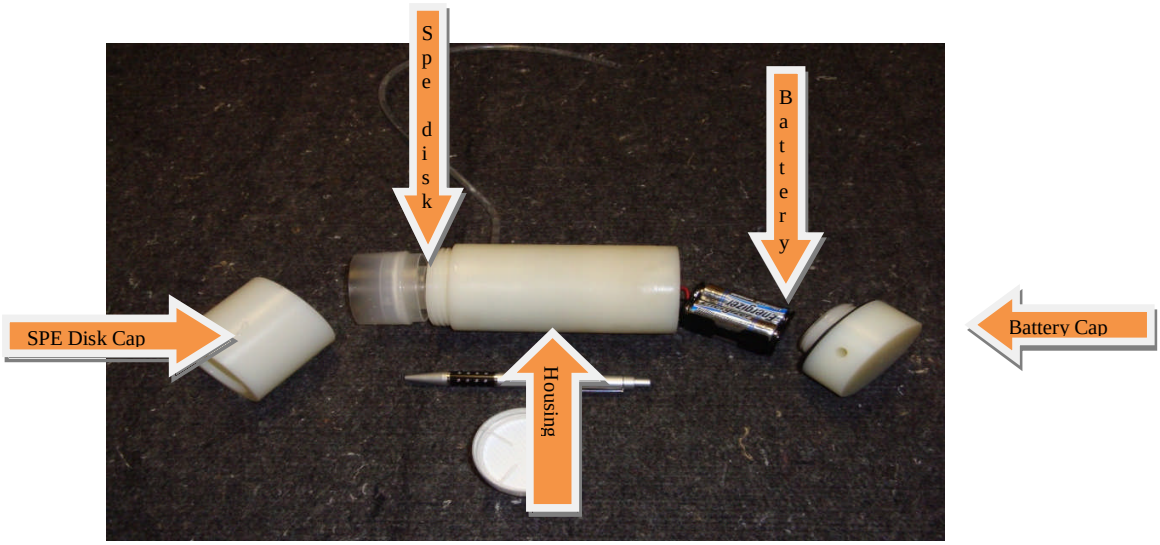
525.2 list of compounds

1. isophorone
2. 2-nitro-*m*-xylene (SS)
3. naphthalene
4. dichlorvos (DDVP)
5. hexachlorocyclopentadi
6. EPTC
7. mevinphos
8. butylate
9. vernolate
10. pebulate
11. etridiazole (Terrazole®)
12. 2,6-dinitrotoluene
13. acenaphthylene
14. acenaphthene-d10 (IS)
15. chlorneb
16. tebuthiuron
17. 2,4-dinitrotoluene
18. molinate
19. fluorene
20. propachlor
21. ethoprop (ethoprophos)
22. cycloate
23. chlorpropham
24. trifluralin
25. atraton
26. hexachlorobenzene
27. prometon
28. simazine
29. atrazine
30. propazine
33. pentachlorophenol
34. terbufos
35. pronamide (propyzamide)
36. diazinon
37. phenanthrene-d10 (IS)
38. phenanthrene
39. disulfoton
40. methyl paraoxon
41. anthracene
42. terbacil
43. chlorothalonil
44. metribuzin
45. simetryn
46. ametryn
47. alachlor
48. prometryn
49. terbutryn
50. bromacil
51. cyanazine (Bladex)
52. metalochlor
53. chlorpyrifos
54. triademefon
55. Dacthal® (DCPA)
56. MGK-264 (isomer A)
57. diphenamid
58. MGK-264 (isomer B)
59. merphos
60. heptachlor epoxide
61. fluoranthene
62. stirofos
63. disulfoton sulfone
65. butachlor
66. pyrene-d10 (SS)
67. fenamiphos
68. pyrene
69. napropamide (Devrinol®)
70. *trans*-nonachlor
71. merphos oxide
72. tricyclazole (Beam)
73. carboxin
74. chlorobenzilate
75. norflurazon
76. bis(2-ethylhexyl) adipate
77. hexazinone (Velpar®)
78. triphenylphosphate (SS)
79. benzo(a)anthracene
80. chrysene-d12 (IS)
81. chrysene
82. bis(2-ethylhexyl)
83. fenarimol
84. *cis*-permethrin
85. trans-permethrin
86. di-*n*-octyl phthalate
87. benzo(b)fluoranthene
88. benzo(k)fluoranthene
89. benzo(a)pyrene
90. fluridone (Sonar®)
91. perylene-d12 (SS)
92. indeno(1,2,3-cd)pyrene
93. dibenzo(a,h)anthracene
94. benzo(ghi)perylene

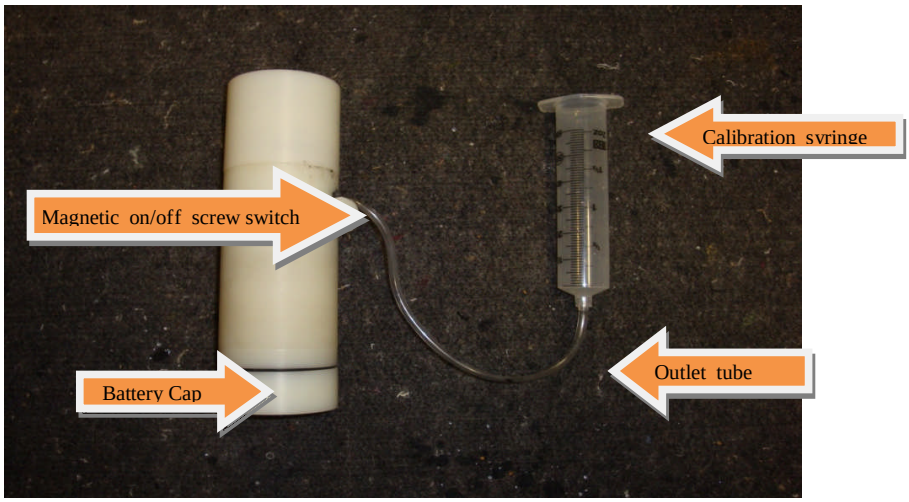
TPH analysis EPA 8015 -Diesel and extended oils

Appendix C

Clam Deployment Instructions



Dissembled View



Assembled view and calibration set up view

Above are photos of the Continuous Low-level Aquatic Monitoring device called the CLAM. It comes assembled with batteries and pre-conditioned SPE disks mounted to the unit. To turn on the unit, simply screw in the magnetic tipped polymer bolt into the housing and it will activate the pump. It should be attached with the filter pointing downstream in any manner that completely restricts free motion. The CLAM should be treated as an instrument and not subjected to severe jolts or rough handling.

The following steps will be a simple guide to turn on, calibrate, deploy, and remove the CLAM and transport the SPE disks to the Laboratory.

STEPS

1. Attach the provided outlet tubing to the outlet barbed connector in the housing; to the other end attach the measuring syringe by pressing the tubing on the end as in picture.

2. Activate the CLAM by screwing in the polymer magnetic tipped bolt until it seats; the pump will then be activated. The Pump will not be hurt by running in air.

3. Submerge the CLAM in the water to be sampled and keep the syringe above the surface. Let the system run for a few minutes to stabilize flow. Holding the disk end up, but still underwater, will help remove entrapped air.

4. Hold the syringe next to the CLAM in a vertical position just out of the water. Empty the syringe volume, hold upright and immediately begin timing. Try to keep the syringe at a level as to not induce too much head on the pump. The syringe can be held partially underwater as long as the tube seal is good.

5. At exactly 1 minute, record the volume collected in the syringe. Repeat for accuracy. Repeat this procedure at the end of the deployment, and possibly at the midpoint. An average flow rate in ml/min can be obtained between each calibration, thus allowing the total volume of water to be computed at the end of the deployment.

6. Remove the syringe from the CLAM. The tubing can be left in place for ease of calibrations.

7. While still activated secure the CLAM to a structure, branch, pipe, or board that will hold the CLAM with the disk housing facing downstream of any flow or oriented away from any sediment sources. Let the unit extract for the time period planned. Be sure to log in the deployment and retrieval time in minutes, hours and days, as this information is critical to the total volume extracted.

8. Unscrew the SPE disk cap and pull off the SPE disk from the seating tube. Also remove the tubing seal on the disks end nipple. Pour out any water in the disk and place the disk in the bag provided, and submit to the laboratory.

9. Do not touch the disk surface with your fingers or gloves, as it will contaminate the media.

10. Unscrew the magnetic polymer bolt and remove, thus deactivating the CLAM.

11. Calibration example: at 8am on day 1 the calibration shows 40ml/min. At 8am on day 2 the calibration shows 30ml/min. At 8am on day 3 the calibration shows 20ml/min and the CLAM is removed. For 24 hours (1440 minutes) the average flow rate was 35ml/min. Then for the next 24 hours (1440 minutes) the average flow rate was 25ml/min. The total volume extracted would be (35 x 1440) + (25 x 1440) = 86,400 ml or 86.4 Liters.

Summary and Results from Campus Spillway and Peters Canyon Reservoir

Procedure Summary;

The deployed disks were sent to Anatek Laboratories in Moscow Idaho, specializing in pesticides analysis using ion trap GC/MC/MS. The disks were eluted with acetone and DCM, dried with sodium sulfate, and then concentrated under a nitrogen stream to a two ml final extract volume. The initial volume of the sample used for the final calculation was the supplied volume in liters from the field extraction event. The standard EPA 8270 internal standards were post spiked into the one ml of the extract. All the extracts were run against a 6 point initial calibration for the Pyrethroid target list found in Appendix B. The 525.2 and TPH were analyzed once at each site for the targets listed also in Appendix B.

Campus Spillway Result Summary:

The Triazine herbicide Simazine was found in all the samples from Campus Spillway site. The values ranged from 89-649 ng/l over a four day sample event. Bromicil was found to also be in this site from a 525.2 single analysis at 44.3 ng/l.
The Campus Spillway site also had a TPH single analysis performed, with a silica gel cleanup to remove any biogenic material, and was found to have 2.38 ug/l Diesel and 4.41 ng/l Lube oil contamination.

Peters Canyon Reservoir Result Summary:

Results from the Peters Canyon Reservoir had no detectable hits from any of the compounds in Appendix B list except for the TPH which was found to have 2.59 ug/l of Diesel and 8.66 ug/l of Lube oil on a single analysis.

Surrogate Recovery and Extraction volume Tables:

Campus Spillway

Date Sampled	Sampler ID	Analyte ng/l	Surr. % Rec	Extract vol. liters
*3-9-10	U1	Simazine 343 ng/l	44.8	48.6
3-9-10	U3	Simazine 679 ng/l Bromacil 44.3 ng/l	72.2	15.2
3-12-10	U2	Simazine 95.2 ng/l	63.4	60.6
3-13-10	U2	*****	*****	26.6
3-18-10	U1	Simazine 89.1 ng/l	104.4	11.9

***** note sample extract volume lost do to breakage in the Laboratory.

*TPH on 3-9-10 had 2.38 ug/l diesel and 4.41 ug/l lube oil range organics

Peters Canyon Reservoir

Date Sampled	Sampler ID	Analyte ng/l	Surr. % Rec	Extract vol. liters
3-22-10	U1	ND	68.0	59.7
*3-22-10	U2	ND	66.6	77.9
3-24-10	U1	ND	39.9	60.0
3-24-10	U2	ND	77.8	36.6
3-25-10	U1	ND	65.6	51.3
3-25-10	U2	ND	43.0	44.8
3-26-10	U1	ND	62.4	37.1
3-26-10	U2	ND	66.6	39.2
3-27-10	U1	ND	101.0	46.8
3-27-10	U2	ND	52.0	37.9
3-29-10	U1	ND	70.0	47.2
3-29-10	U2	ND	65.2	35.4
3-30-10	U1	ND	70.0	47.2
3-30-10	U2	ND	54.2	29.3
3-31-10	U1	ND	43.4	47.6
3-31-10	U2	ND	71.0	34.7

***TPH on 3-24-10 had 2.59 ug/l diesel and 8.66 lube oil range organics.**

Conclusions:

Each of the disks that were sent to the field were spiked with 100ul of 100 mg/l surrogate of Terphenly-d14 which was recovered within the prescribed control limits of 20-120%. The observed recovery range for the surrogate was a low of 39% to a high of 104%, and was matrix or extraction dependent, and not correlated to the volume extracted. The 525.2 analysis run once at each site were targeted for pesticides, PAH's and PCP. It should be noted that the units expressed were in ng/l or parts per trillion for the pesticides, and ug/l or parts per billion for the TPH analysis. Standard reporting limits for 525.2 and pyrethroid analysis is ug/l or parts per billion and TPH is mg/l or parts per million for a standard liter grab sample. The RL was 10 ng/l for samples of 40 liters or more, based on 5 times the low point of the ICAL curve. Lower reporting levels could be obtained by running a 7 point MDL study on spiked disks.

When the Analysis and data from the POCIS and SMPE is available a full data review and summary will be made available.