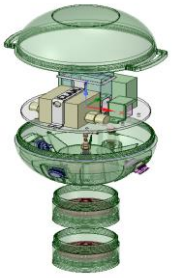
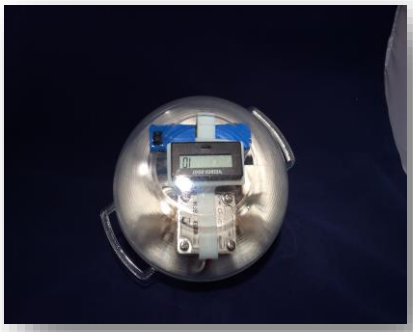
# A Laboratory Study Comparing SPE Time Integrated Field Extractions to SPE Laboratory Extractions for Non-Polar Analytes

Continuous low level aquatic monitoring device called the CLAM, has been developed to provide a time integrated sample held within a solid phase extraction disk that represents a day or weeks of continuous submersible integrated sampling. The patented design allows the submersible CLAM to draw the water through the SPE media disk first, preventing hydrophilic analytes from adhering onto the tubing and pump surfaces.



The CLAM overcomes the grab samples "snapshot in time" stigma, by providing a quantitative continuous sampling event for hours to weeks, sequestering episodic events and dynamic changes in the aquatic environment. The CLAM also provides enhanced sensitivity by integrating up to one hundred liters of water into one SPE disk, which has been field extracted for laboratory elution and analysis.

The CLAM is compact, 2.5 inches by 8 inches, submersible to hundreds of feet, and runs on 4 AA batteries for days to weeks, dependent on the model. The device can be enclosed in stealth enclosures, such as resin rocks or limbs, or adapted with special OEM designed SPE disks to continuously sample low flow storm water. The SPE disk media can be specific for non-polar analytics, polar compounds and chelating resin disks to sequester multivalent metal cations all at a neutral pH.



Laboratory comparison bench studies were conducted to determine the extraction efficacy of a SPE laboratory grab sample extraction, to the CLAM extraction, for both precision and sensitivity for; Organochlorine Pesticides, PAH's and Permerthrin. One hundred twenty liters of distilled water pH 5.9 was spike to 0.1 ug/l solution concentration with Pesticides, PAH's and Permerthrin. The spiked volume was mixed with a circulating submersible pump without concern for analytes adhering onto the walls of the vessel. A one liter grab sample was taken by pumping the spiked water into the bottle until full. The water was then pumped in 12 liter aliquots into receiving jars, which submersed the CLAM sampler. A 10 liter extraction event and a 100 liter sampling event were conducted within the 12 liter receiving jar using additions as the level was depleted. The in situ extraction was performed using the high flow rate model, using 70 ml/min extraction rate over 2.4 hours for the 10 liter event, and 24 hours for the 100 liter event. The exact volume passing through the CLAM was collected in a second vessel, which correlated to the pumping rate. (See Picture).

The SPE extraction disk used for both the CLAM and the laboratory was a DVB H2O phobic phase for non-polar and slightly polar analytes. Both disks were preconditioned with methanol and then washed with pH 2 water before use. The laboratory grab sample was adjusted to a pH 2.0 before extracting, while the CLAM extraction was performed in the neutral pH environment of 5.9 of the distilled water in the receiving vessel. After the SPE extraction, both the laboratory and the CLAM extraction disks were vacuumed dry, and eluted with 10 ml of DCM into 40 ml vials. The extracts were dried with Na2SO4 and adjusted to 10 ml final volume.

Analysis of the extracts was performed using an Ion-Trap GC/MS with a DB-5ms 30 M x 0.25 x 0.25 GC column. One ml aliquot's of the 10 ml extract was placed into 1ml auto sampler vials and internal standards were added to the extracts. The analysis was performed as an SW846-8270 analysis for semi volatiles. The results of the analysis are listed in tabular format. The extract solution concentrations are reported in ug/l, and the calculated water concentrations are reported in ug/l, for the one liter grab sample, the 10 liter and 100 liter CLAM extracted samples.

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Results from the GC/MS analysis for the PAH analysis of the laboratory SPE extracted grab sample, and the CLAM extracted sample, expressed in ug/l. are listed in tables below.

| PAH Analysis Results in ug/l | 1 liter grab Extract conc. | 1 liter grab Water conc. | 10 liter CLAM Extract conc. | 10 liter CLAM Water conc. | 100 liter CLAM Extract conc. | 100 liter CLAM Water conc. |
|---|---|---|---|---|---|---|
| Naphthalene | 16.74 | 0.167 | 110.18 | 0.110 | 849.51 | 0.085 |
| 2-Methylnaphthalene | 11.39 | 0.114 | 91.85 | 0.092 | 748.37 | 0.078 |
| 1-Methylnaphthalene | 9.18 | 0.092 | 84.37 | 0.084 | 857.32 | 0.087 |
| Acenaphthylene | 7.45 | 0.075 | 92.54 | 0.093 | 995.39 | 0.099 |
| Acenaphthene | 12.40 | 0.124 | 83.88 | 0.084 | 847.70 | 0.085 |
| Fluorene | 9.23 | 0.092 | 80.39 | 0.080 | 796.29 | 0.080 |
| Phenanthrene | 9.77 | 0.098 | 102.31 | 0.102 | 854.45 | 0.085 |
| Anthracene | 7.85 | 0.079 | 71.78 | 0.072 | 778.58 | 0.078 |
| Fluoranthene | 14.51 | 0.145 | 121.63 | 0.122 | 972.99 | 0.097 |
| Pyrene | 12.18 | 0.122 | 102.90 | 0.103 | 748.82 | 0.075 |
| Benzo(a)anthracene | 9.75 | 0.098 | 100.84 | 0.101 | 821.36 | 0.082 |
| Chrysene | 11.83 | 0.118 | 109.05 | 0.109 | 1124.80 | 0.112 |
| Benzofluoranthenes | 15.15 | 0.152 | 141.78 | 0.141 | 1004.22 | 0.104 |
| Benzo(a)pyrene | 5.34 | 0.053 | 51.79 | 0.052 | 265.66 | 0.027 |
| Indeno(1,2,3-cd)pyrene | 4.27 | 0.043 | 21.38 | 0.024 | 212.79 | 0.021 |
| Dibenz(a,h)anthracene | 2.45 | 0.025 | 22.06 | 0.022 | 281.42 | 0.028 |
| Benzo(g,h,i)perylene | 5.62 | 0.056 | 23.73 | 0.024 | 223.86 | 0.022 |
| **Pesticide Analysis Results in ug/l** | **1 liter grab Extract conc.** | **1 liter grab Water conc.** | **10 liter CLAM Extract conc.** | **10 liter CLAM Water conc.** | **100 liter CLAM Extract conc.** | **100 liter CLAM Water conc.** |
| alpha-BHC | 10.03 | 0.100 | 81.20 | 0.081 | 815.43 | 0.082 |
| beta-BHC | 10.37 | 0.103 | 73.24 | 0.073 | 907.53 | 0.091 |
| delta-BHC | 14.13 | 0.141 | 103.94 | 0.104 | 1034.26 | 0.103 |
| gamma-BHC | 12.26 | 0.123 | 112.56 | 0.113 | 919.08 | 0.092 |
| Heptachlor | 9.64 | 0.096 | 88.51 | 0.089 | 677.26 | 0.068 |
| Aldrin | 8.08 | 0.081 | 63.08 | 0.063 | 630.10 | 0.063 |
| Heptachlor epoxide | 11.15 | 0.112 | 106.13 | 0.106 | 805.92 | 0.081 |
| gamma-Chlordane | 9.46 | 0.095 | 73.16 | 0.073 | 690.24 | 0.069 |
| Endosulfan I | 9.45 | 0.095 | 85.78 | 0.086 | 807.19 | 0.081 |
| DDE | 8.26 | 0.083 | 73.22 | 0.073 | 650.82 | 0.065 |
| Dieldrin | 11.41 | 0.114 | 107.10 | 0.107 | 755.84 | 0.076 |
| Endrin | 17.76 | 0.178 | 124.03 | 0.124 | 706.30 | 0.071 |
| Endosulfan II | 6.14 | 0.061 | 107.09 | 0.107 | 984.75 | 0.098 |
| DDD | 10.24 | 0.102 | 99.06 | 0.099 | 704.62 | 0.070 |
| Endrin aldehyde | 9.75 | 0.098 | 72.69 | 0.073 | 1215.36 | 0.122 |
| DDT | 8.34 | 0.083 | 70.39 | 0.070 | 626.61 | 0.063 |
| Endosulfan Sulfate | 12.17 | 0.122 | 93.42 | 0.093 | 753.48 | 0.075 |
| Endrin ketone | 14.31 | 0.143 | 92.69 | 0.093 | 671.15 | 0.067 |
| Methoxychlor | 8.08 | 0.081 | 94.55 | 0.095 | 998.06 | 0.100 |
| Permethrin | 8.06 | 0.081 | 75.62 | 0.076 | 558.29 | 0.056 |

**Results and Conclusion**: Observations of the data shows a lowering of the water concentration values. from the grab sample to the 10 and 100 liter clam extracted samples. This is due to the fact that the analytes had a longer residence time in the receiving jar and the mixing tank, 2.4 hours for the 10 liter CLAM sample and 24 hours for the 100 liter Clam sample. The fact that non-polar compounds will adhere to container surface walls is well known, here we are measuring dynamics of surface adhesion in a closed system. This is well illustrated in the analysis of the very hydrophilic PAH's , note the last five PAH's. These compounds have a very high Kow, the resultant recoveries show a 80 percent loss of these analytes onto the vessel and pump walls. These compounds are also the most carcinogenic, and accuracy is of great importance.

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In the real world, the aquatic environment is not contained in bottles, to sample it accurately the water must not contact any vessel, tubing or pump which isn't extracted and combined into the extract representing the sample. The CLAM is the only continuous sampler which extracts the sample first before contact with any tubing and pump, providing a continuous time integrated sample that is orders of magnitude lower in detection as can be seen in the extract ug/l comparison.