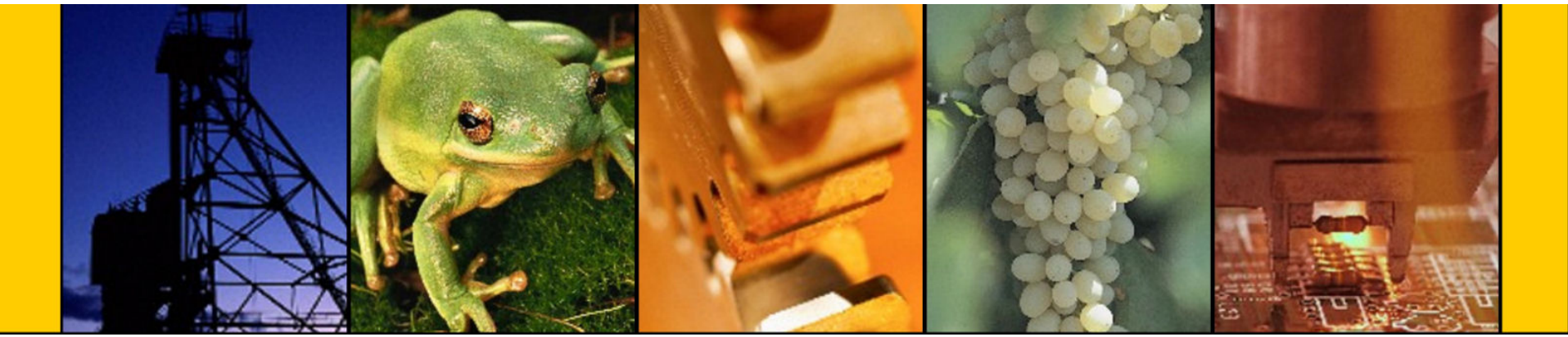
ALS Laboratory Group

ANALYTICAL CHEMISTRY & TESTING SERVICES

Special Chemistries Division



Presentation Title: Sample Hold Time Evaluation for Polycyclic Aromatic Hydrocarbons in Water Samples

by: D.A. Birkholz and Jarrod Roberts

Right solutions….

….Right partner

Acknowledgements

- ALS Laboratory Group for funding this study
- ALS Special Chemistries for doing the work (Dr. Ralitsch)
- Chris Lange, ALS Edmonton, sample collection
- Lori Cormier, Jackie Kunka and Heather Amyotte sample extraction, concentration
- Andrea Hage and Jarrod Roberts GC/MS analysis, data interpretation, reporting
- Michelle Breland review and statistics

Renewed Interest in PAHs

- **Toxicological focus both in terms of environmental and human health**
- **Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms (EPA-600-R-02-013. Requires the analysis for 34 PAHs including homologues**
- **Potency Equivalency Factors (PEFs) for Carcinogenic Polycyclic Aromatic Hydrocarbons (Health Canada, 2006). Requires the analysis for 44 PAHs including homologues**
- **PEFs included in Federal Contaminated Site Risk Assessment in Canada: Guidance on Human Health Preliminary Quantitative Risk Assessment (Health Canada, 2007).**
- **PAHs are prime candidates for source tracking (forensics)**

US – EPA Sample Holding Time Reevaluation

- “Sample hold time reevaluation” October 2005, EPA/600/R-05/124
- SW-846 prescribed upper bound for allowable variability between replicates for semi-volatile organic compound extraction is coefficient of variation (CV) ≤ 25%
- Holding time recommended for soils/sediments under SW-846 is 14-days and for waters 7-days.
- Following a reassessment, holding time for sediments held at -20^{o}C is 138-days (9.8 * MHT)

Objective of this work

- Determine if the MHT (7-days) for water (SW-846) was defensible
- Determine if the use of preservatives could extend such holding times
- Determine if differing water sources, namely: slough water, river water, groundwater and lake water had an impact on PAH stability

Methods

- Water samples were obtained from the following sources:
- Slough (Northern Bear golf course)
- River (N. Saskatchewan river, Rossdale Water Treatment Plant raw water intake)
- Lake (Lake Wabamun)
- Groundwater (acreage)

Methods

- Samples were fortified with PAHs at the 1 ug/L level
- Some samples were preserved with ascorbic acid (0.4 g/L), copper sulfate (5 mL/L, 10% w/v) and sulfuric acid (5 mL/L, 6N)
- Samples were analyzed on day 0, day 7 and day 21
- Non-spiked (control) samples were analyzed as well
- Surrogates were added prior to extraction including: nitrobenzene-d5; 2-fluorobiphenyl and p-terphenyl-d14
- Water samples (1L) were processed using EPA SW-846 method 8270
- Analyses performed using gas chromatography/mass spectrometry – selected ion-monitoring

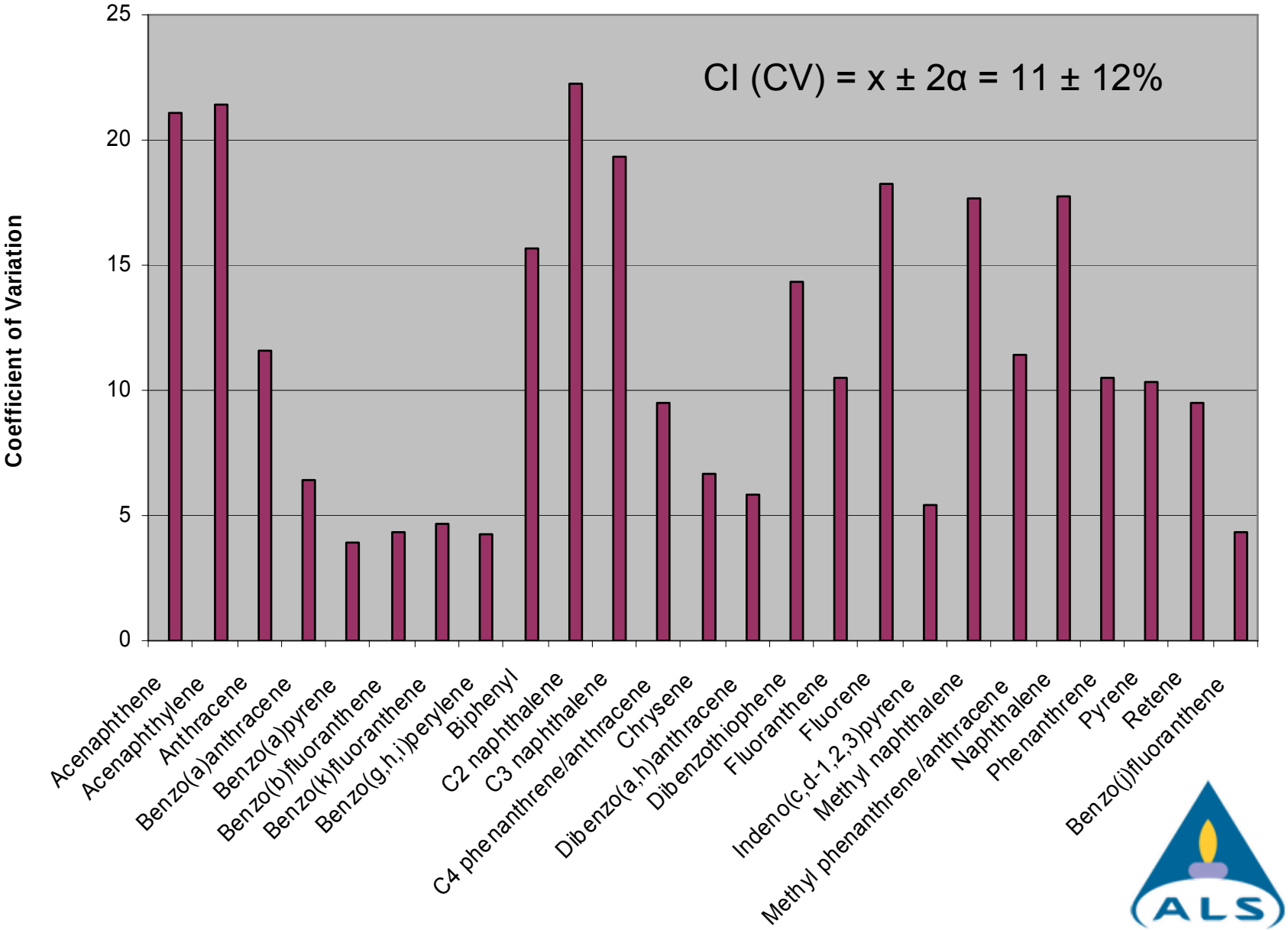
PAHs sought

acenaphthene	acenaphthylene	anthracene
benzo(a)anthracene	benzo(a)pyrene	benzo(b)fluoranthene
benzo(k)fluoranthene	benzo(g,h,i)perylene	biphenyl
1,3-dimethyl-naphthalene	2,3,5-trimethyl-naphthalene	C4-phenanthrene
chrysene	dibenzo(a,h)anthracene	dibenzothiophene
fluoranthene	fluorene	indeno(1,2,3,-cd)pyrene
1 - methyl naphthalene	2-methyl naphthalene	naphthalene
phenanthrene	pyrene	retene
benzo(j)fluoranthene	2-methyl anthracene	
	26-compounds	

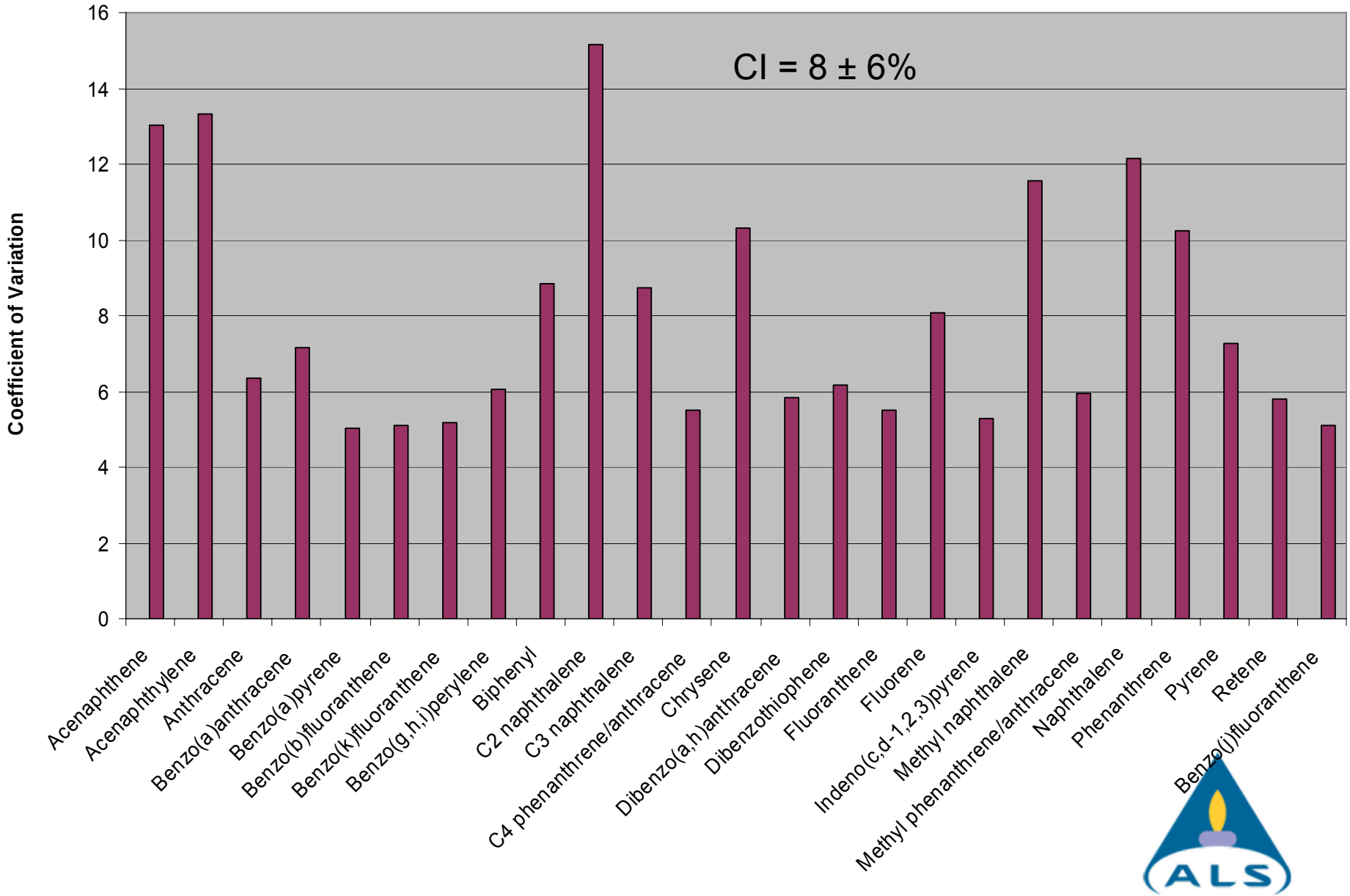
Statistics

- Mean, standard deviation, and coefficient of variation (RSD%) were obtained for all analytes
- Percent reduction of analytes from day 0 was determined
- Average percent reduction along with coefficient of variation was determined
- Successful treatment was viewed if mean reduction was less than 25% from D0

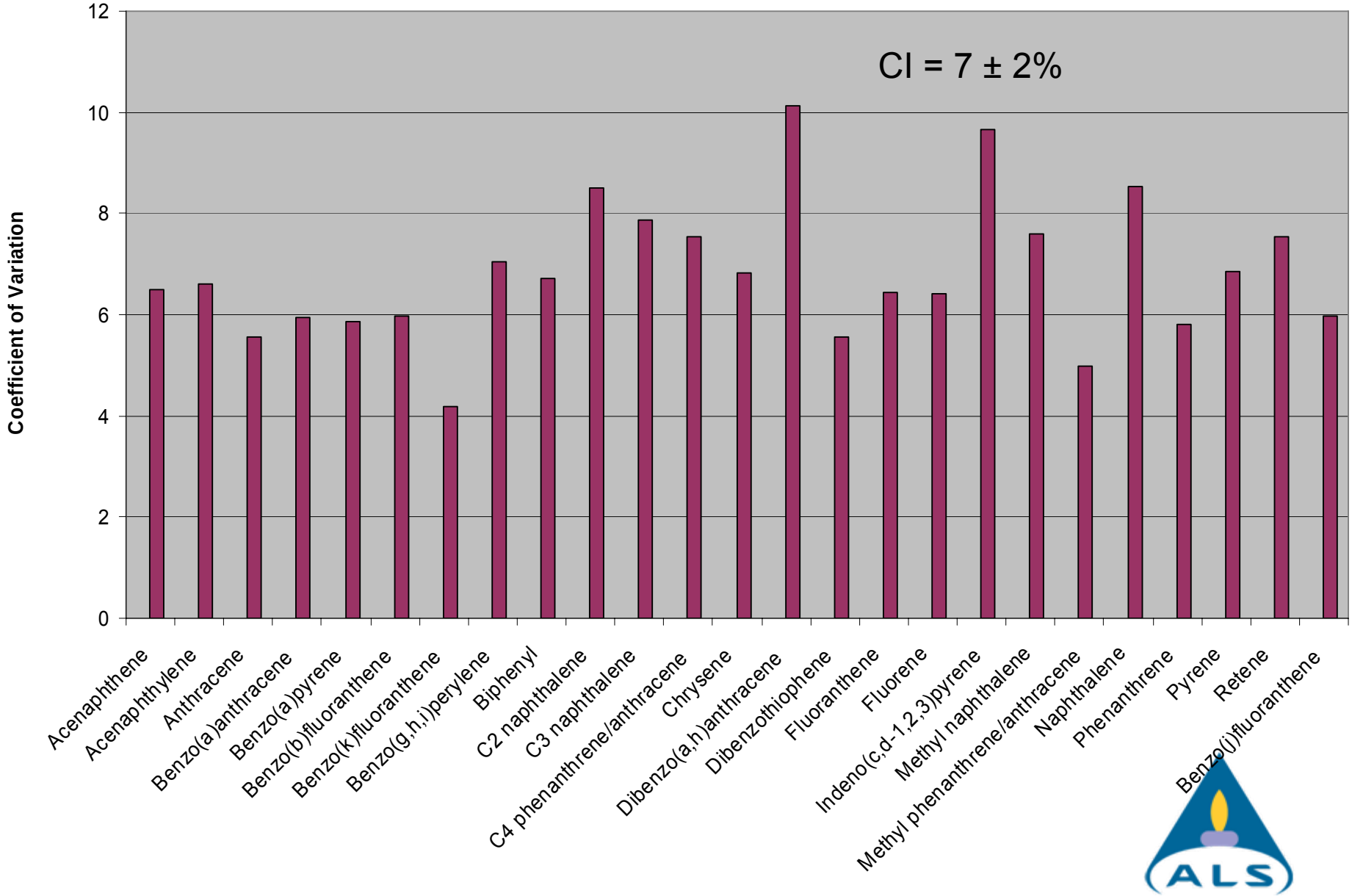
D0 River Water (n = 8)



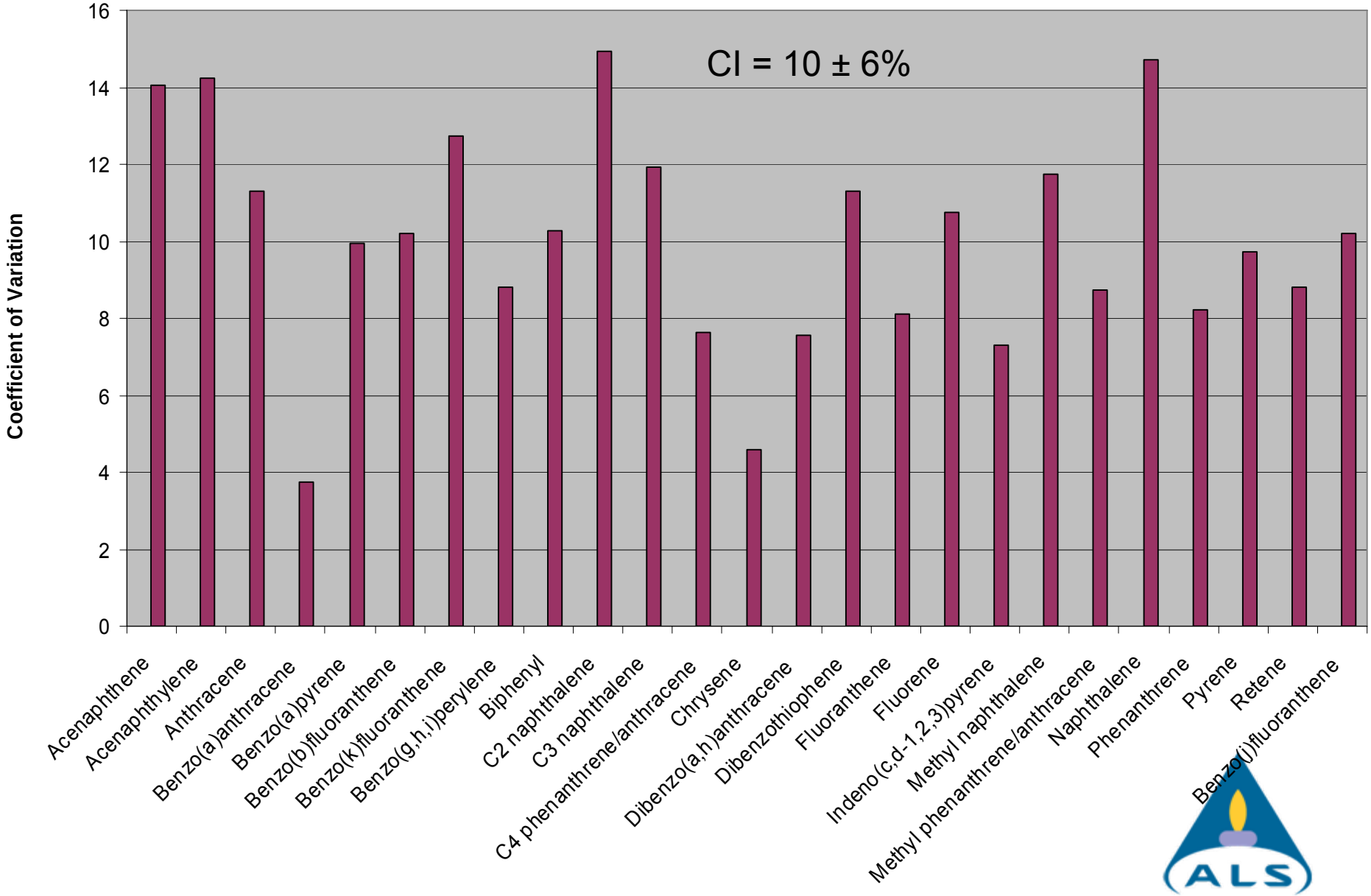
D0 Lake Water n = 8



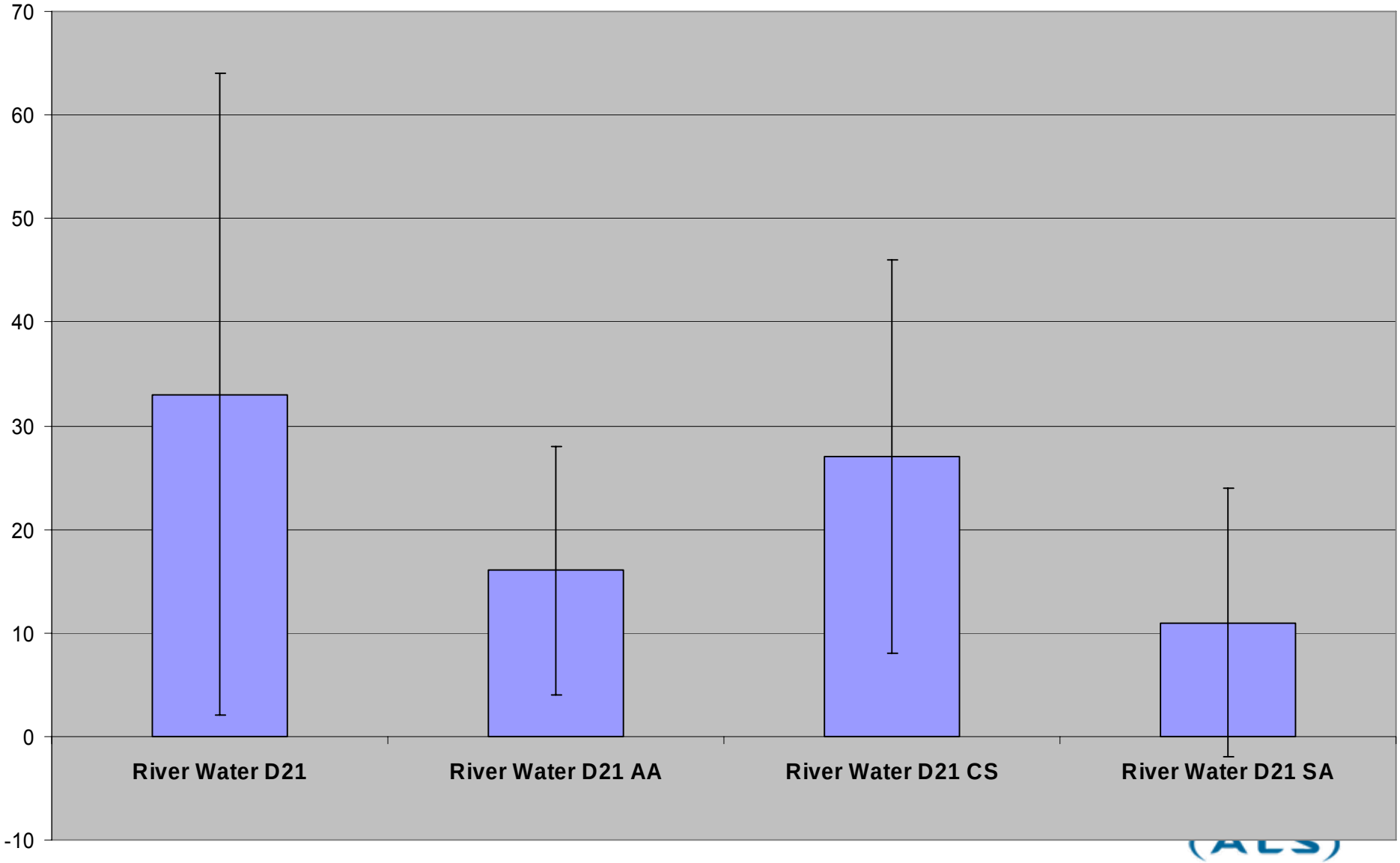
D0 Slough Water n = 8



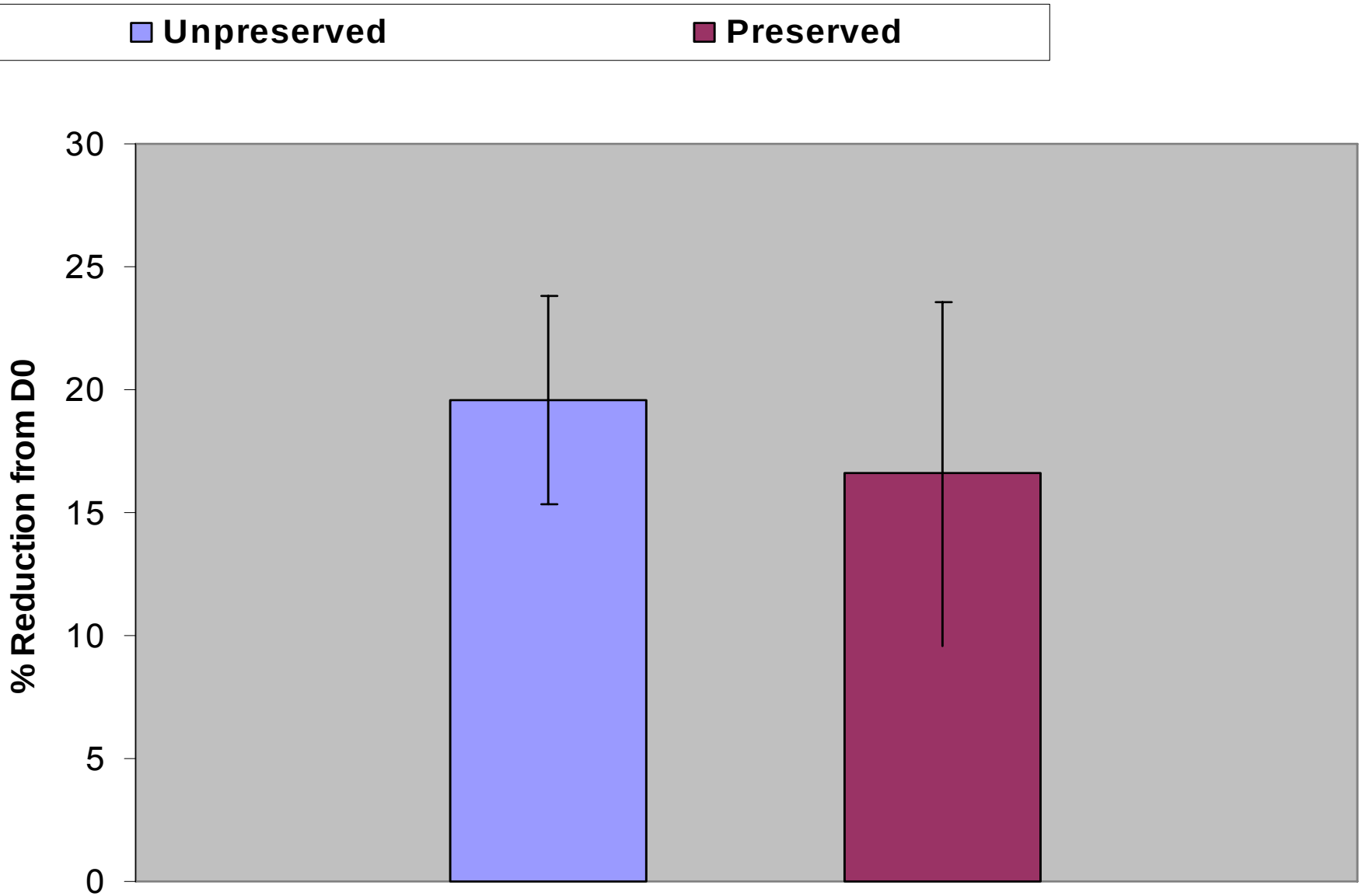
D0 Groundwater n = 8



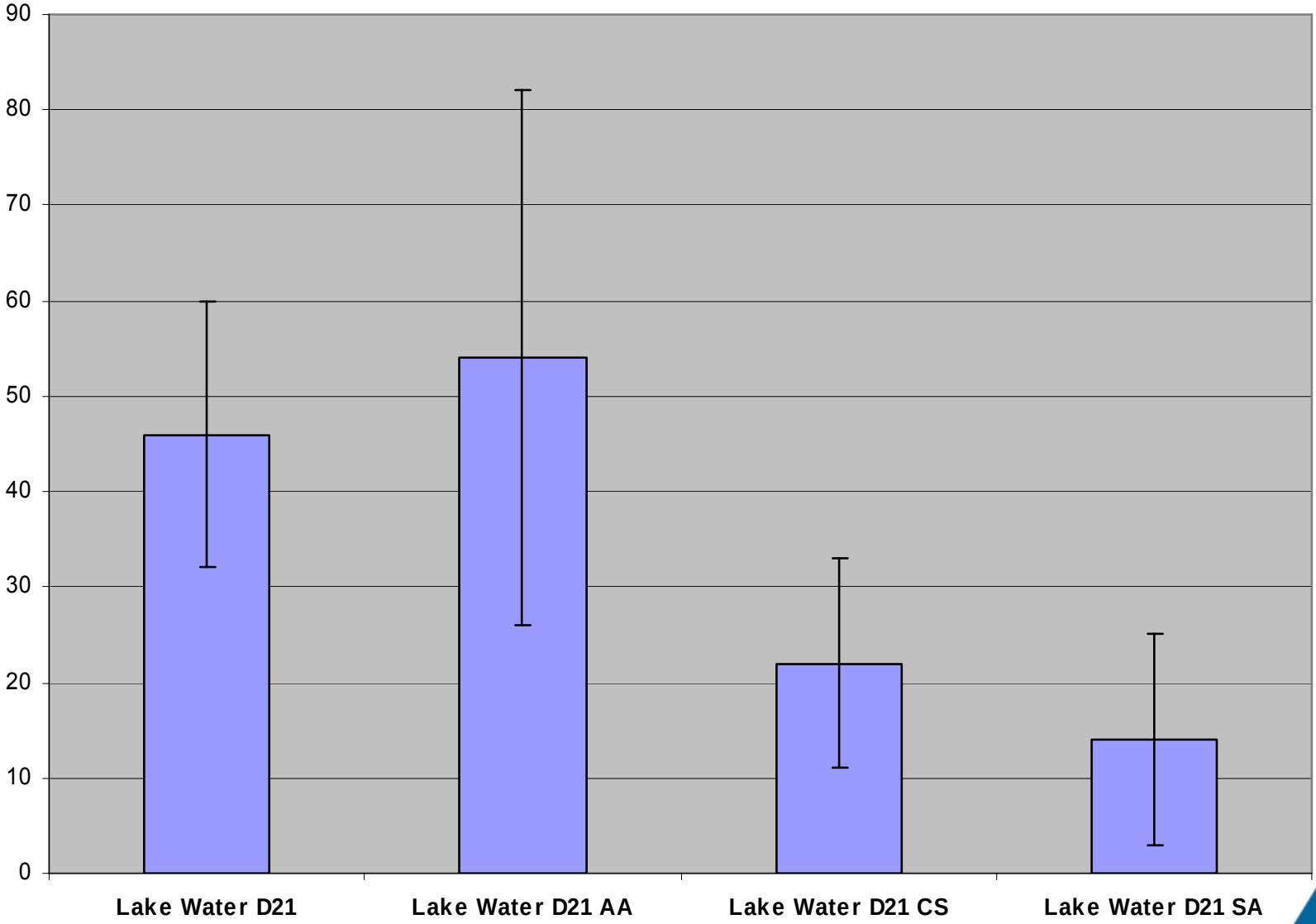
River Water D21: % PAH Reduction from D0

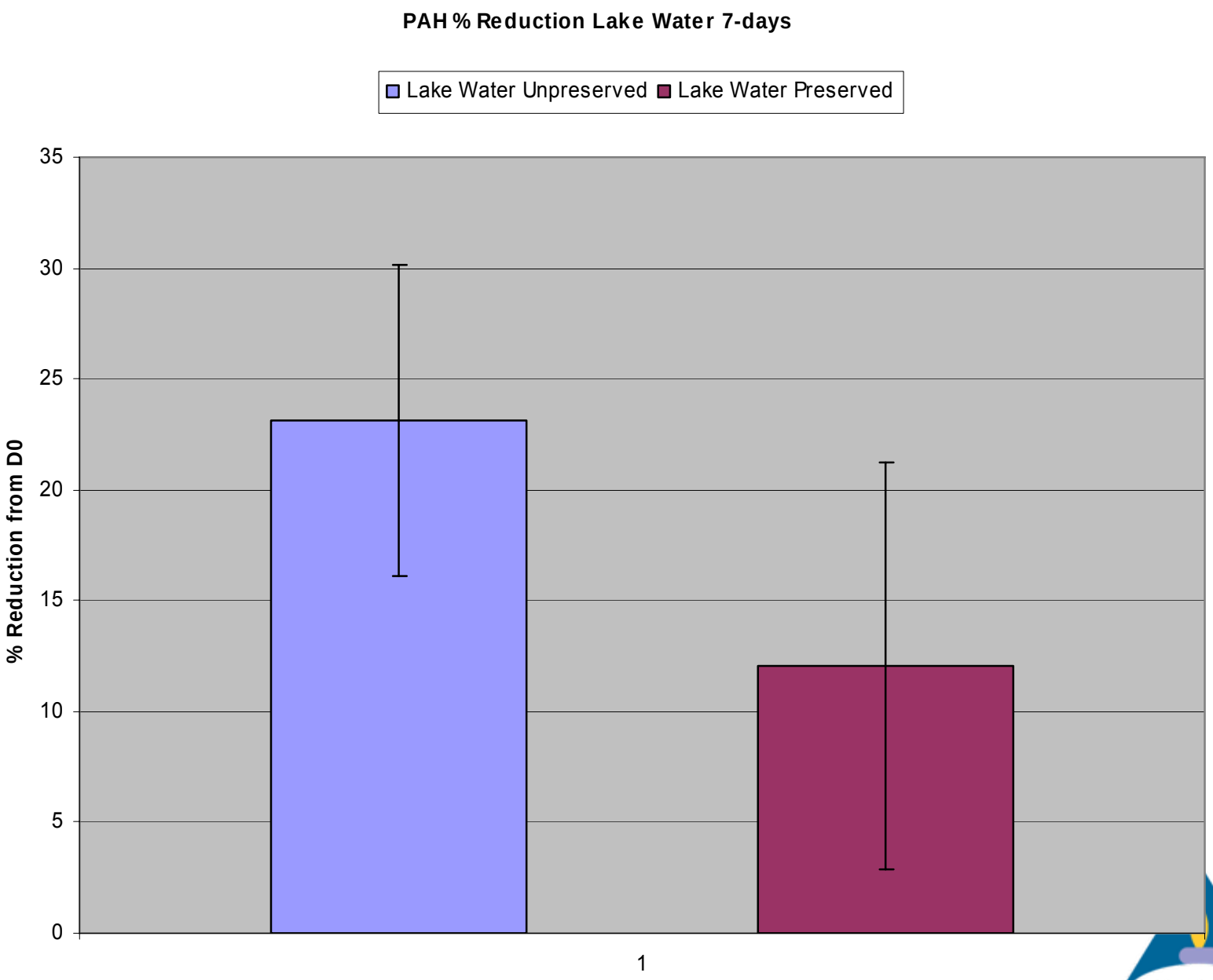


% PAH Reduction River Water 7 - Days

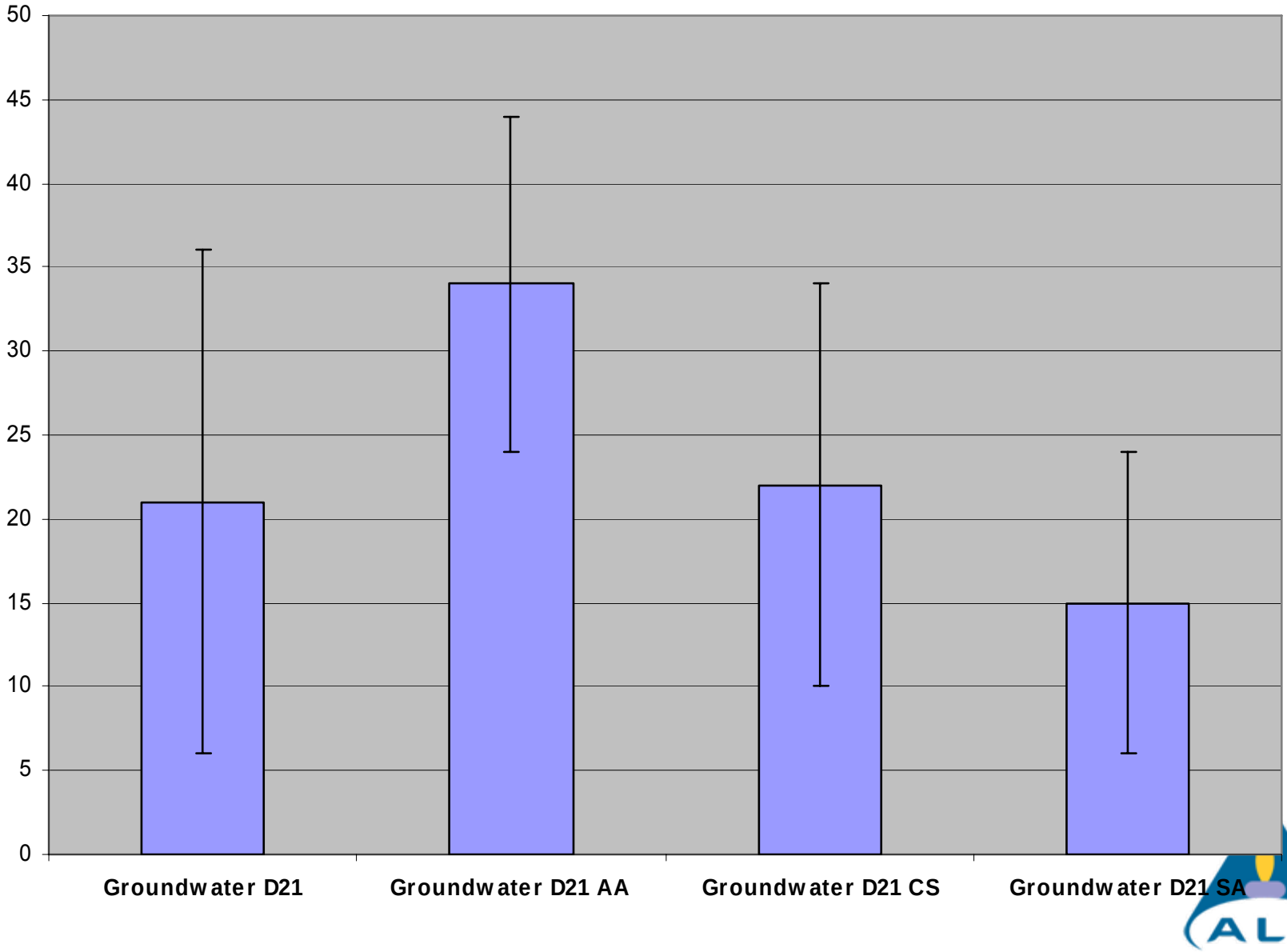


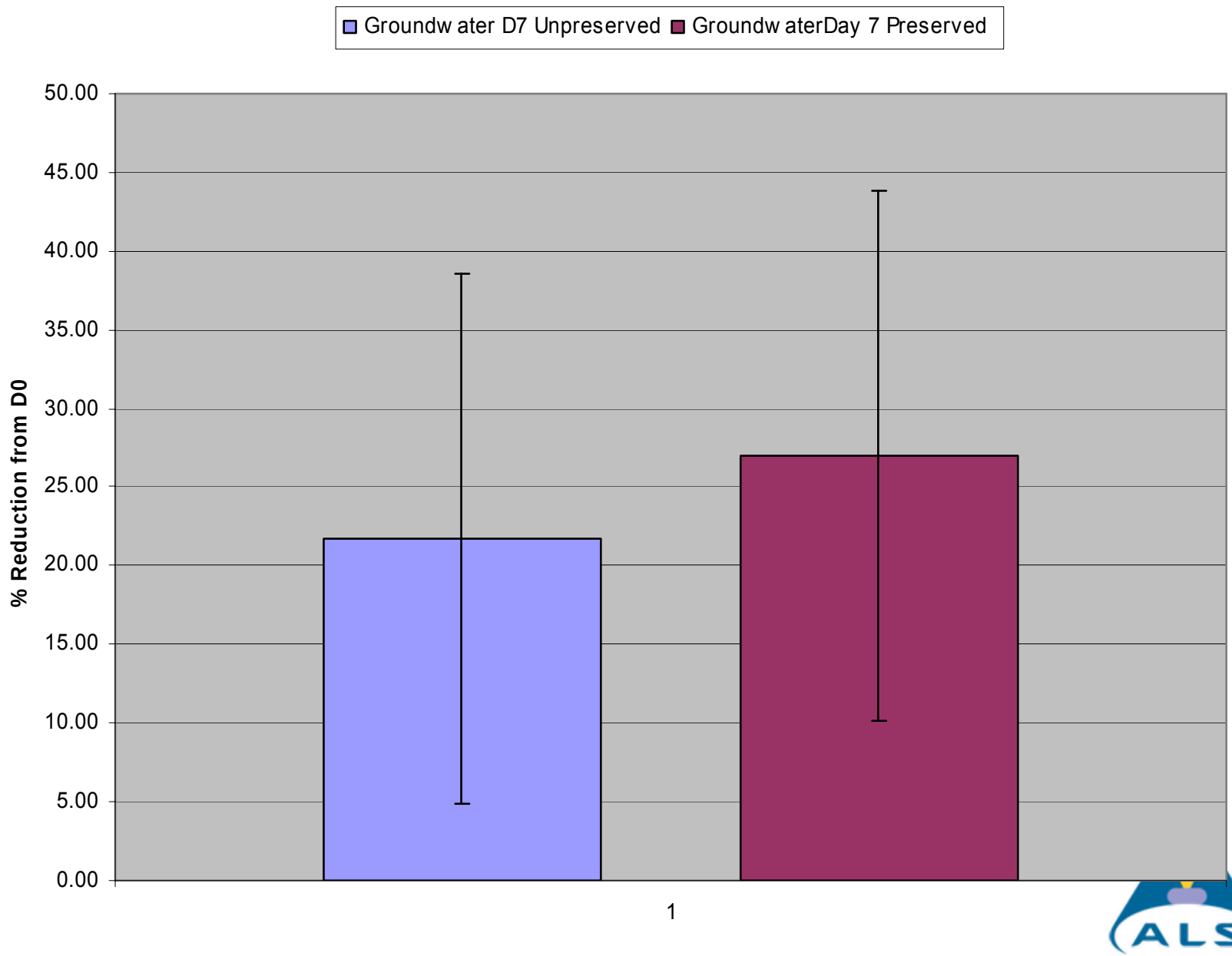
Lake Water D21: % PAH Reduction from D0



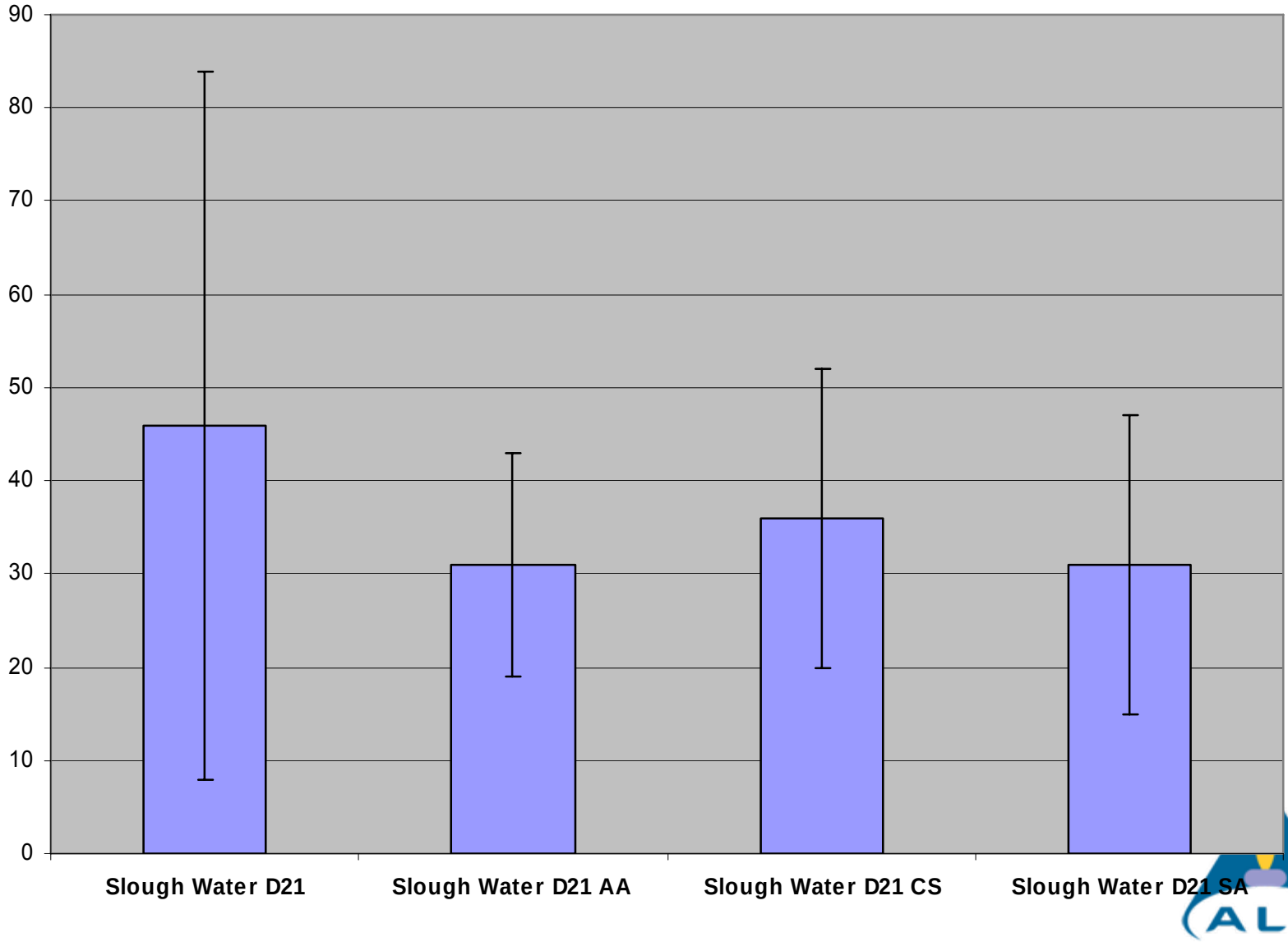

PAH % Reduction Lake Water 7-days
Lake Water Unpreserved
Lake Water Preserved
% Reduction from D0
35
30
25
20
15
10
5
0
1

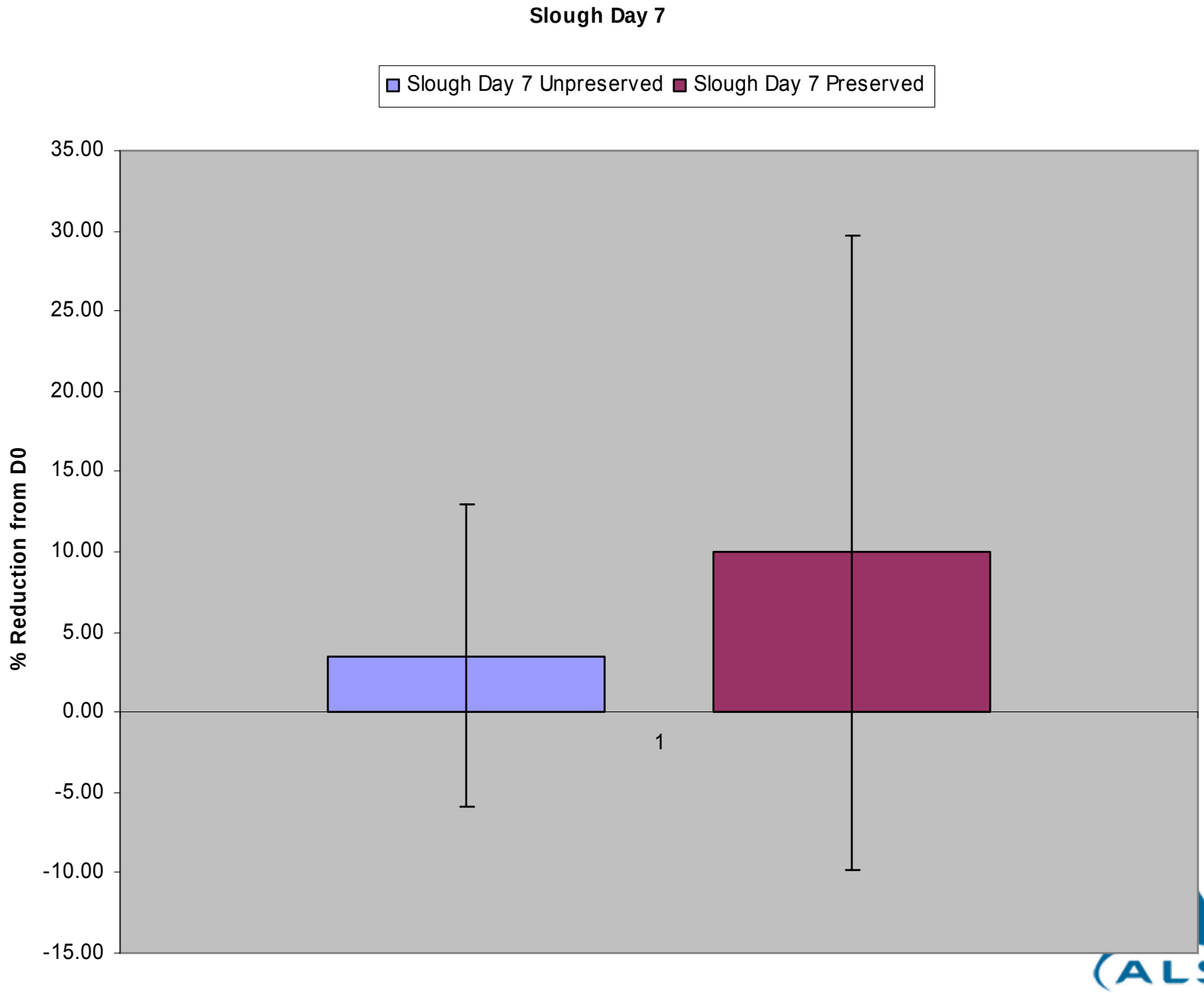
Groundwater D21: % PAH Reduction from D0



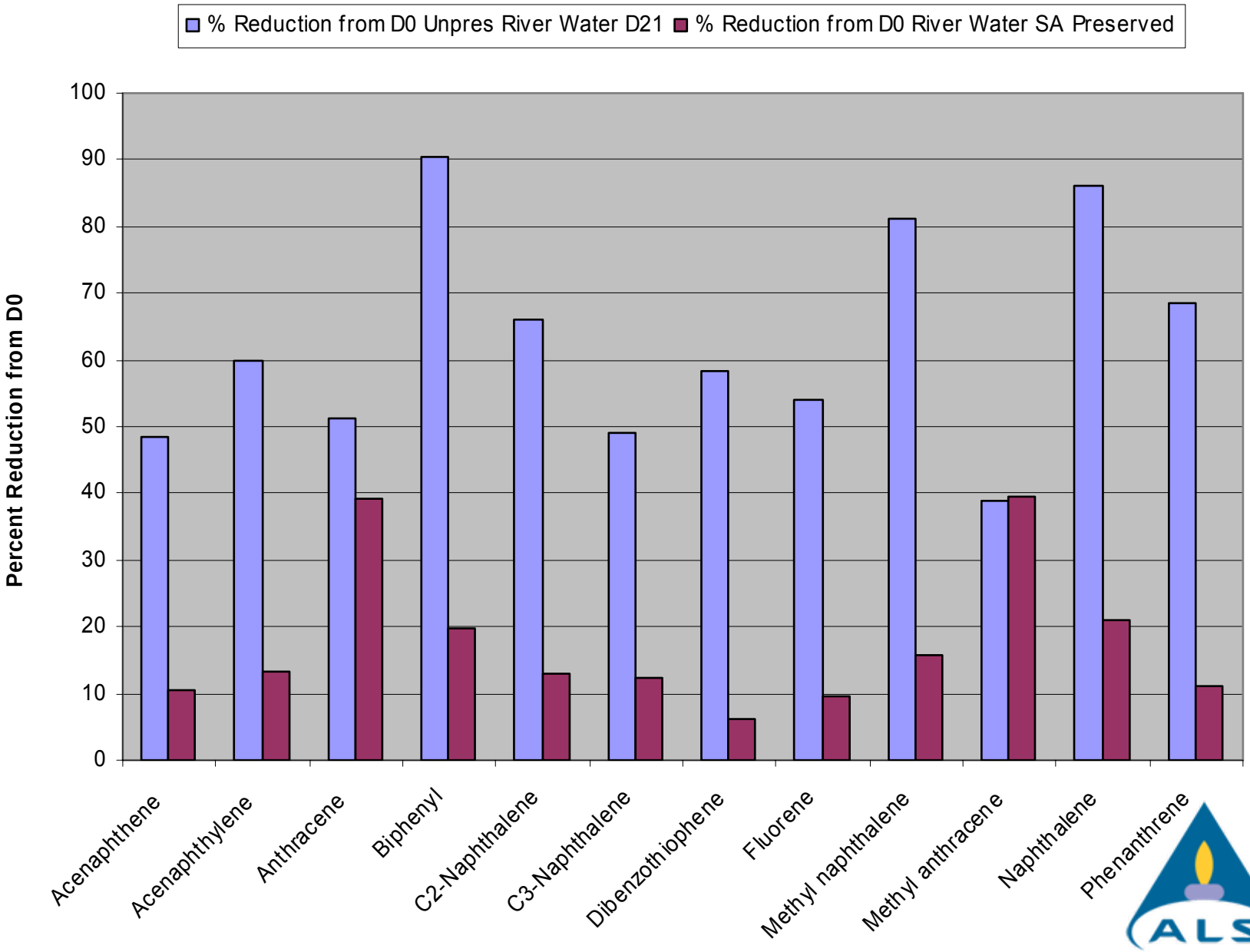

Groundwater Day 7
Groundwater D7 Unpreserved
GroundwaterDay 7 Preserved
50.00
45.00
40.00
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
% Reduction from D0
1

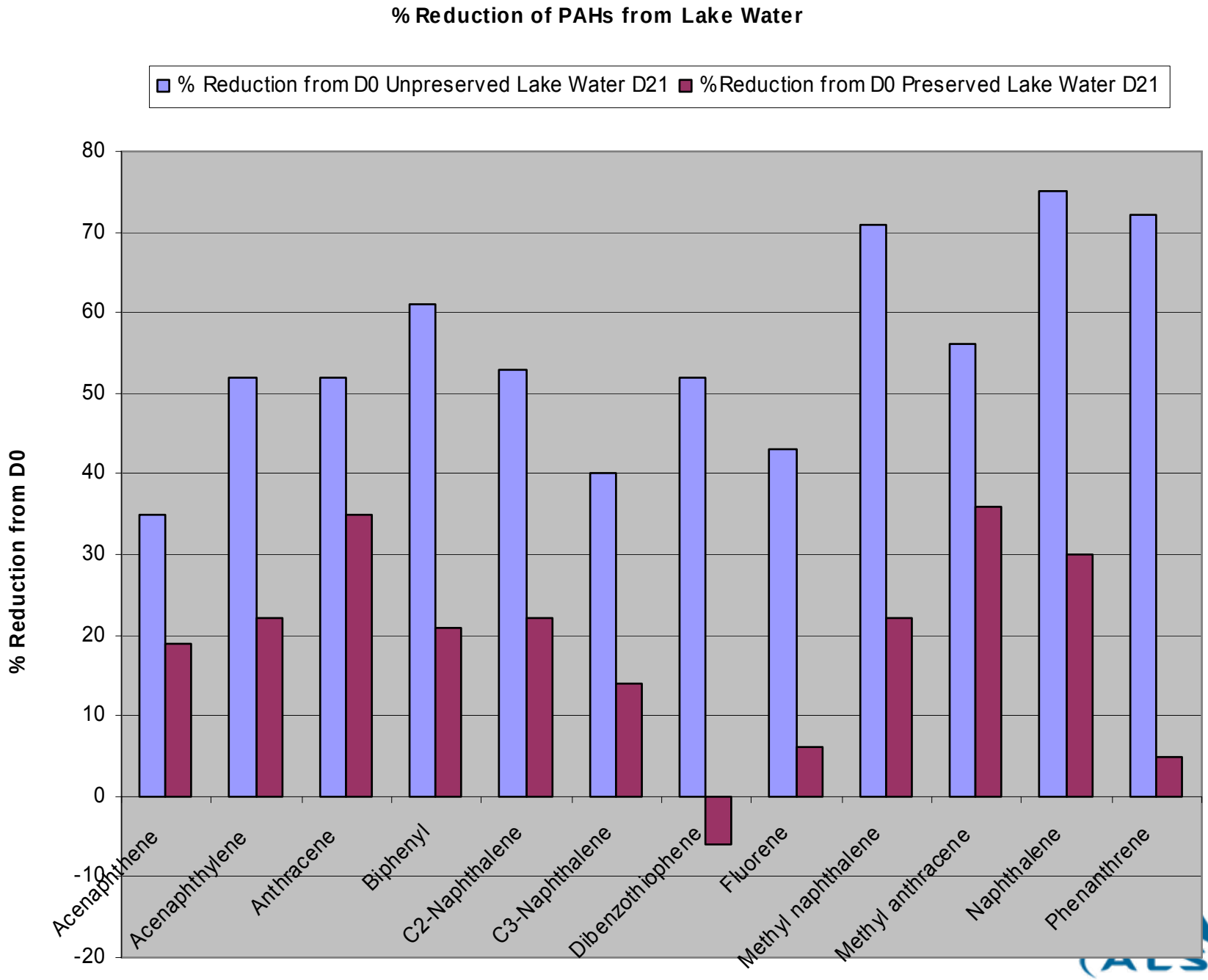
Slough Water D21: % PAH Reduction from D0

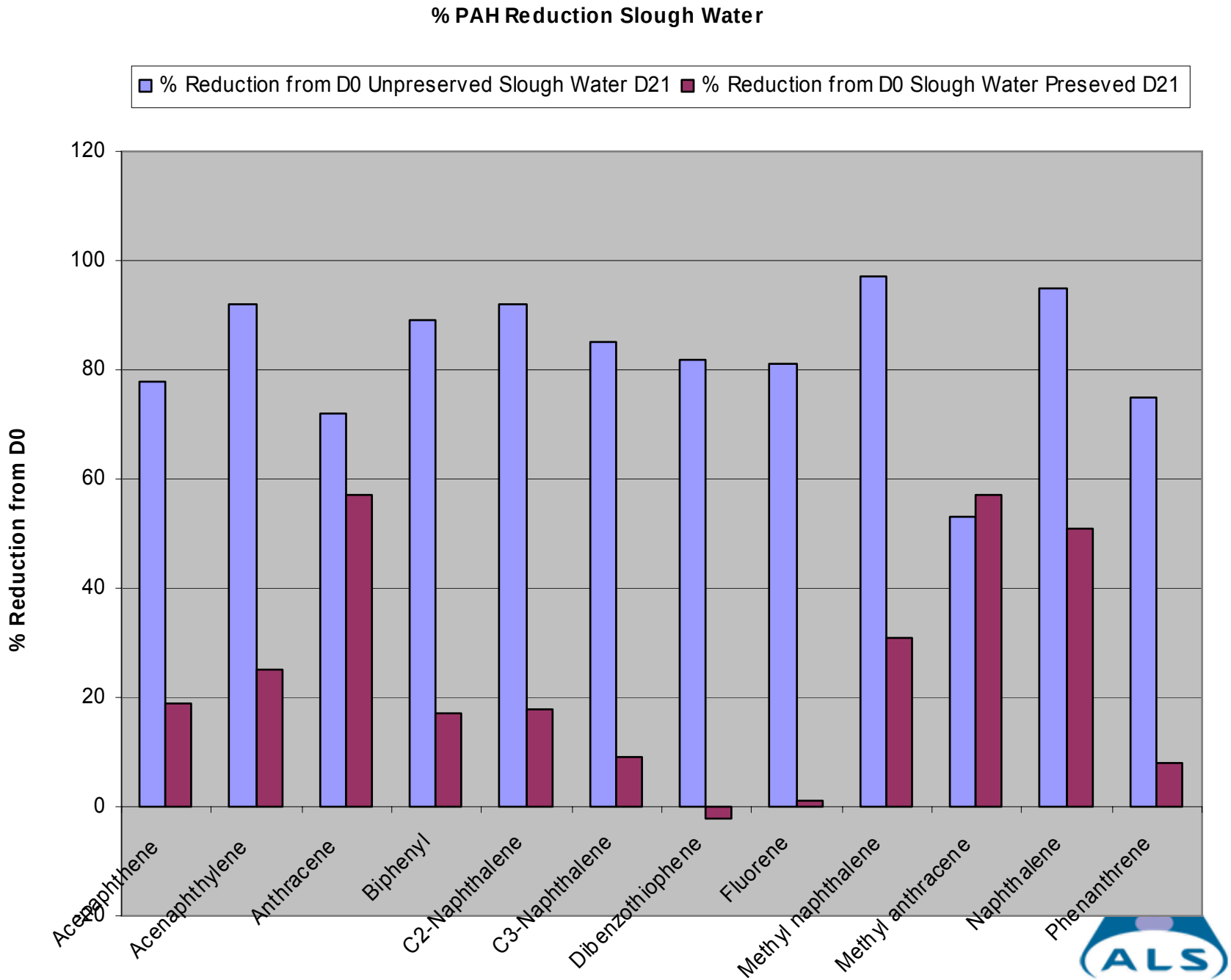


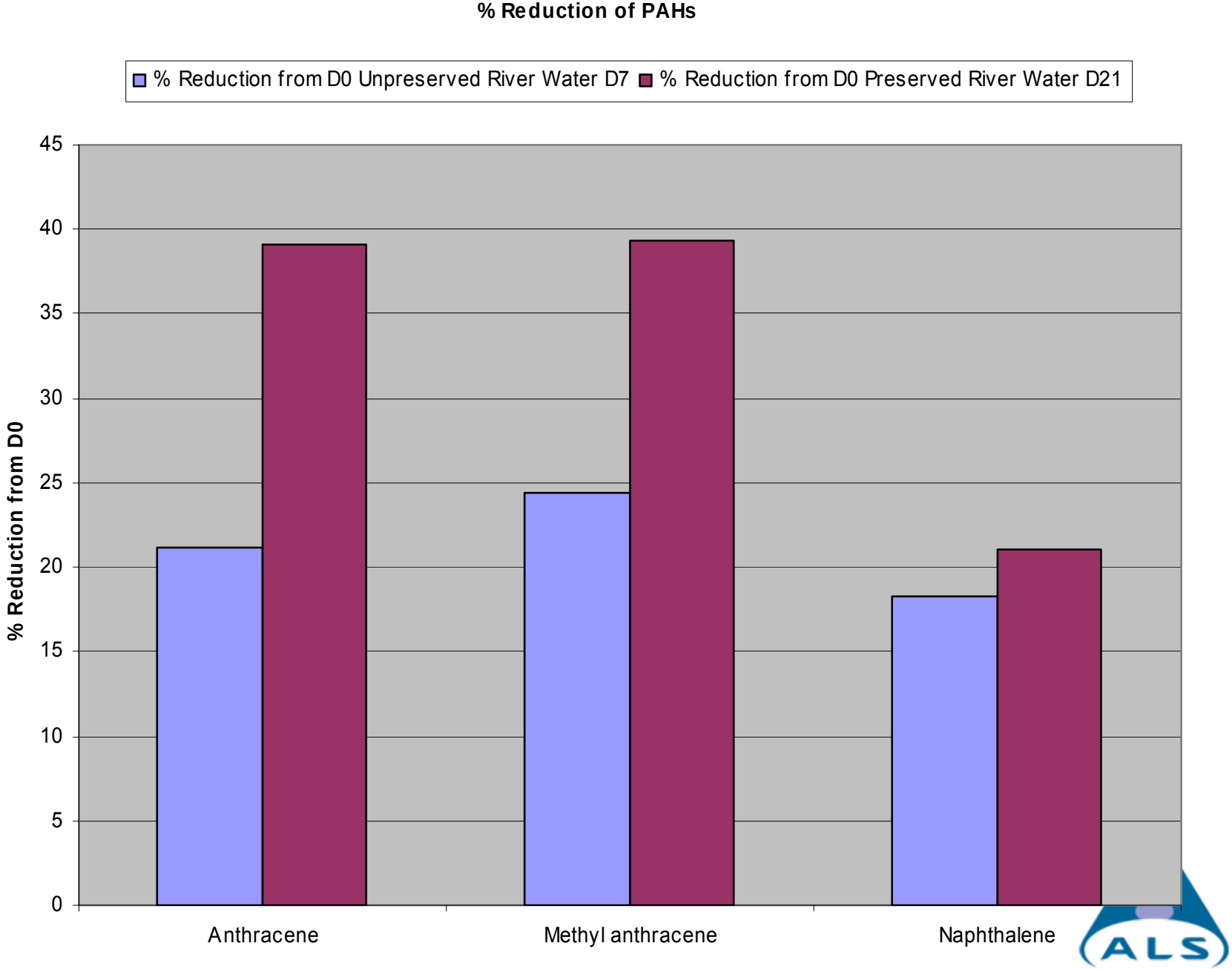

Slough Day 7
Slough Day 7 Unpreserved
Slough Day 7 Preserved
% Reduction from D0
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
-5.00
-10.00
-15.00
1

Effect of Preservation on Select PAHs




% Reduction of PAHs from Lake Water
% Reduction from D0 Unpreserved Lake Water D21
%Reduction from D0 Preserved Lake Water D21
% Reduction from D0
80
70
60
50
40
30
20
10
0
-10
-20
Acenaphthene
Acenaphthylene
Anthracene
Biphenyl
C2-Naphthalene
C3-Naphthalene
Dibenzothiophene
Fluorene
Methyl naphthalene
Methyl anthracene
Naphthalene
Phenanthrene


% PAH Reduction Slough Water
% Reduction from D0 Unpreserved Slough Water D21
% Reduction from D0 Slough Water Preseved D21
% Reduction from D0
120
100
80
60
40
20
0
Acenaphthene
Acenaphthylene
Anthracene
Biphenyl
C2-Naphthalene
C3-Naphthalene
Dibenzothiophene
Fluorene
Methyl naphthalene
Methyl anthracene
Naphthalene
Phenanthrene


% Reduction of PAHs
% Reduction from D0 Unpreserved River Water D7
% Reduction from D0 Preserved River Water D21
% Reduction from D0
45
40
35
30
25
20
15
10
5
0
Anthracene
Methyl anthracene
Naphthalene

Problem PAHs

- Anthracene and methyl anthracene are not stable even after preservation, 39% reduction from D0 for both
- The potency equivalency factor (PEF) for anthracene and methyl anthracene is 0 so they are of no consequence in human health risk assessments
- Anthracene and methyl anthracene are near the CV limit of 25% after seven day storage, 21 and 24% reduction, respectively
- The CCME ambient water criteria for anthracene is 4 ug/L chronic and 0.1 ug/L in the presence of light (phototoxic).
- Our preservation method would underestimate toxicity by a factor of two for these two analytes only.

Conclusions

- SW-846 coefficient of variation of 25% for semi-volatile compounds (such as PAHs) was proven valid
- Upper bound confidence intervals for the CVs were: river water (23%); lake water (14%); slough water (9%); and groundwater (16%)
- % PAH reduction from day 0 in river water was 33 ± 31% after 21-days storage at 4^{o}C, and 20 ± 4% after 7-days storage
- % PAH reduction from day 0 in river water was 11 ± 13% after 21-days storage when preserved with sulfuric acid.

Conclusions

- %PAH reduction from day 0 in lake water was 46 ± 14% after 21-days storage and 23 ± 7% after 7-days storage
- %PAH reduction from day 0 in lake water was 14 ± 11% after 21-days storage when preserved with sulfuric acid
- %PAH reduction from day 0 in slough water was 46 ± 38% after 21-days storage and 4 ± 9% after 7-days storage
- %PAH reduction from day 0 in slough water was 31 ± 16% after 21-days storage when preserved with sulfuric acid

Conclusions

- %PAH reduction from day 0 in groundwater was 21 ± 15% after 21-days storage and 22 ± 17% after 7-days storage
- %PAH reduction from day 0 in groundwater was 15 ± 9% after 21-days storage when preserved with sulfuric acid

Conclusions

- Anthracene and methyl anthracene degrade even after preservation.
- From a human health perspective this is of no consequence because the PEF is 0
- Anthracene is important with respect to ambient water criteria.
- Our preservation method would underestimate anthracene by a factor of 2.
- Other that this we feel our preservation method has merit in extending the holding of PAHs, including the alkylated homologues from 7 to 21 days.