

ESTABLISHING A METHOD FOR EXTRACTION OF POLYCYCLIC AROMATIC HYDROCARBONS FROM CONTAMINATED BMP SOILS

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OUTLINE

- Introduction
 - Background
 - Objectives
 - Methodology
 - Results
 - Conclusions
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INTRODUCTION (I)

- Polycyclic Aromatic Hydrocarbons (PAHs)
 - Storm water runoff contains a variety of pollutants that impact the quality of surface water, and ground water
 - Automobiles exhaust deposition
 - Motor oil
 - Pavement seal coats
 - Toxicity
 - Human oral toxicity: 50 – 2000 mg/kg
 - Suggested MCL: 0.2 ppb (Benzo (a) pyrene)*
 - OSHA: limit of 0.2 g/m³ of PAHs*
 - Probable human carcinogens (high molecular weight compounds)



INTRODUCTION (II)

Stormwater runoff Best Management Practices (BMPs)

- State-of-the-art measures
 - Environmentally responsible methods
 - Reduce the release of pollutants to water
-
- Non-Structural BMPs
 - Structural BMPs
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- Retention systems such as wet ponds



“ The significance of storm water runoff in affecting water quality in the United States has become an increasing concern in recent years” (EPA, 1999)

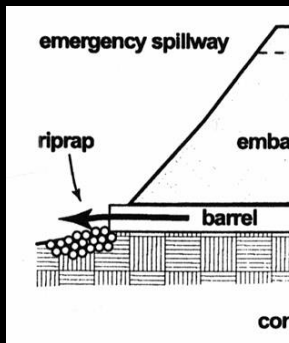


Fig. Dry pond design,



Fig. Dry pond .

Source: NPDES - EPA



Fig. wet pond.

Source: NPDES - EPA

Objectives

Objective

Determine the optimum test procedure for extraction of PAH's from contaminated soils using sonication.

Task 1

Analysis of the different combinations time vs. solvent concentration.

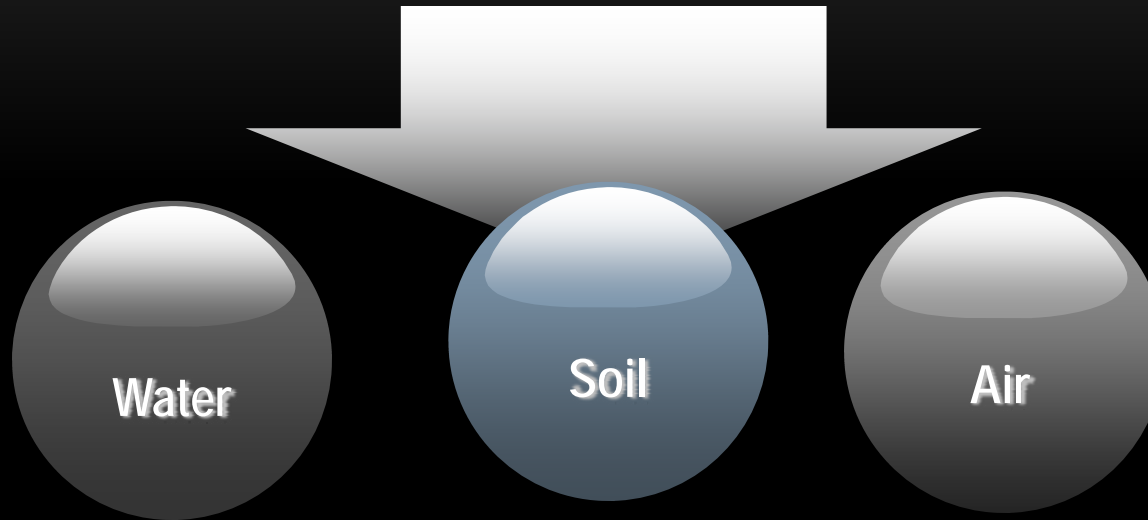
Task 2

Determine the effectiveness of the best combination.

Hypothesis

It is possible to increase the extraction of PAHs from contaminated soils using sonication by optimizing the ratio of solvents and sonication time

Fate and transport of PAHs in runoff from highways



Research guideline:

- Literature review
- Establishing the extraction method
- Establishing the solvents
- Laboratory tests
- Analysis and conclusions

Methodology

PROCESS DIAGRAM

Sampling

- Grained soil (sand)
- $\approx .5 \text{ mg/g}^*$

Sonication

- Cole Palmer
- 55000 herz

Decanting

Centrig.

- 20 min
- 2000 rpm

GC-MS

- Shimadzu
- 30 meter
- 0.25 mmID



EXPERIMENTAL MATRIX

		Sonication Time (min)		
		45	60	75
Ratio A:D	1:3	2	2	2
	1:4	2	2	2
	1:5	2	2	2

Table: Experimental matrix Sonication time versus ratio Acetone (A) and Dichloromethane (D).

		Sonication Time (min)		
		45	60	75
Solvent	A	2	2	2
	D	2	2	2

Table: Experimental matrix Sonication time versus ratio Acetone (A) OR Dichloromethane (D).

EXPERIMENTAL DESIGN

2 Factors

Comparison of the responses for
each combination

Fixed effects model

**FACTORIAL
EXPERIMENT
DESIGN**

$$y_{ijk} = \mu + \tau_i + \beta_j + \tau\beta_{ij} + \epsilon$$

$$\sum_{i=1}^a \sum_{j=1}^b \sum_{k=1}^n (y_{ijk} - \bar{y})^2$$

Statistical data analysis : two way ANOVA

$$SS_T = SS_A + SS_B + SS_{AB} + SSE$$

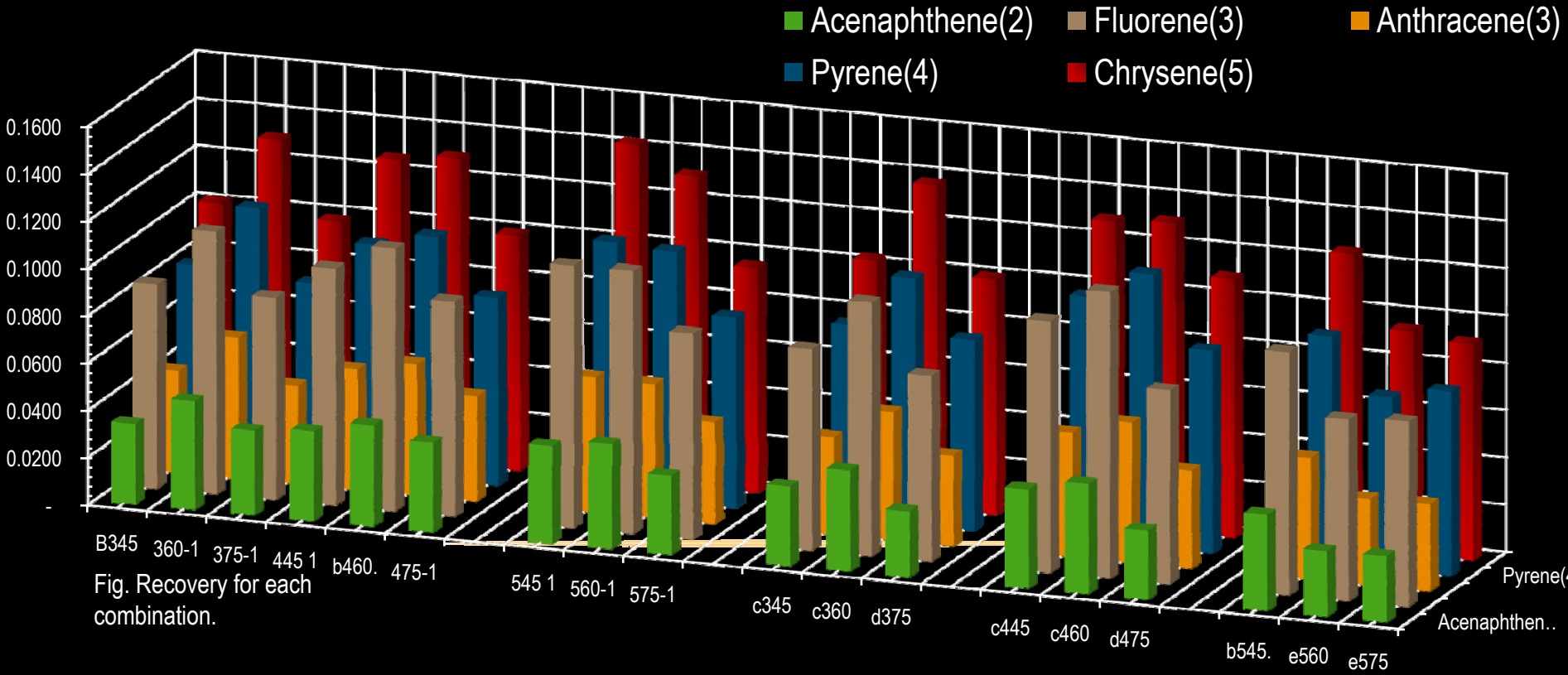
RESULTS

Compound	Average concentration mg/g		
	1:3	1:4	1:5
Acenaphthene	0.0367	0.0394	0.0359
Fluorene	0.0924	0.1020	0.0945
Anthracene	0.0466	0.0509	0.0470
Pyrene	0.0891	0.0975	0.0904
Chrysene	0.1117	0.1208	0.1134

Table: Average recovery for each ratio.

Compound	Average concentration %		
	1:3	1:4	1:5
Acenaphthene	85%	91%	83%
Fluorene	207%	228%	211%
Anthracene	74%	81%	75%
Pyrene	116%	126%	117%
Chrysene	159%	172%	161%

Table: Comparison of Average recovery with other recovery methods. (preliminary values)



ANOVA - TWO-FACTORS WITH REPLICATION

Matrix Chrysene	Factor B Time			
		45	60	75
Factor A Ratio A:D	1:3	0.1012	0.1305	0.0982
		0.1032	0.1374	0.0999
	1:4	0.1266	0.1297	0.0994
		0.1291	0.1307	0.1095
	1:5	0.1426	0.1315	0.0952
		0.1249	0.0945	0.0915

Matrix Acenaphthene				
		45	60	75
factor A Ratio A:D	1:3	0.0340	0.0460	0.0358
		0.0337	0.0428	0.0279
	1:4	0.0380	0.0428	0.0379
		0.0419	0.0466	0.0292
	1:5	0.0412	0.0444	0.0334
		0.0406	0.0278	0.0280

Source	DF	SS	F	P-values
Ratio A:D	2	0.000283	1.37	0.302
Time	2	0.002467	11.93	0.003
Interaction	4	0.001462	3.53	0.054

Source	DF	SS	F	P-values
Ratio A:D	2	4.05E-05	0.76	0.497
Time	2	0.00029	5.41	0.029
Interaction	4	0.000123	1.15	0.395

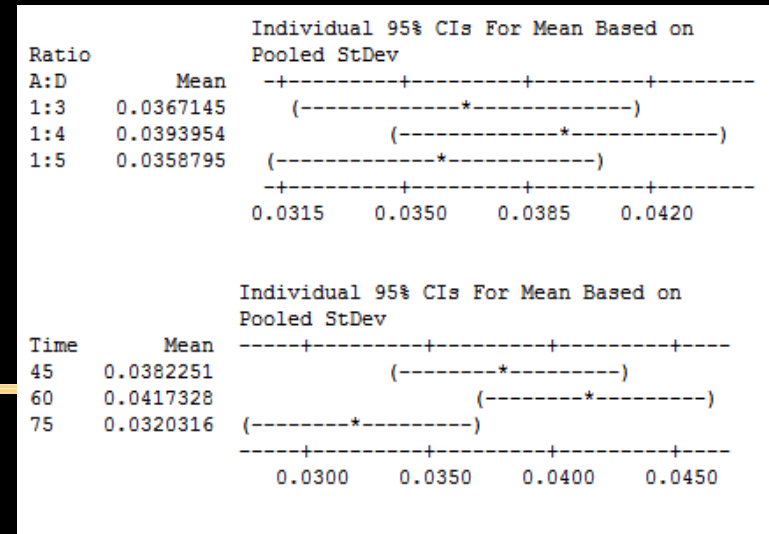
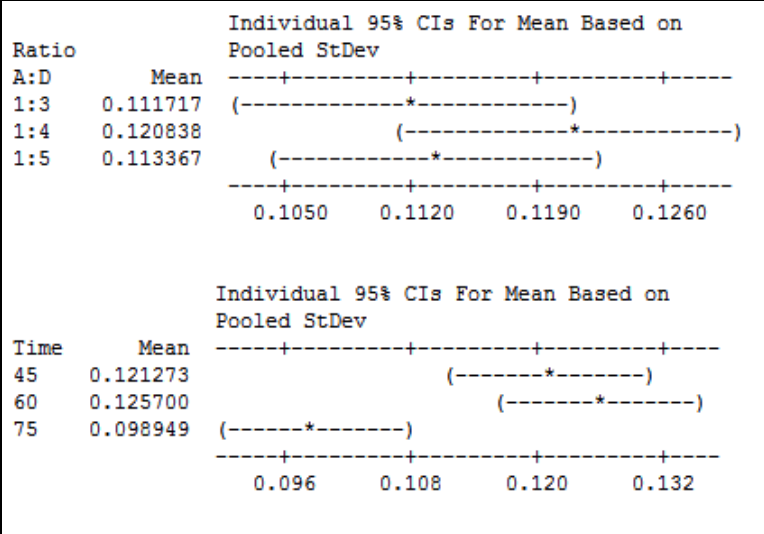


Fig. Statistical data Analysis

ANOVA - TWO-FACTORS WITH REPLICATION

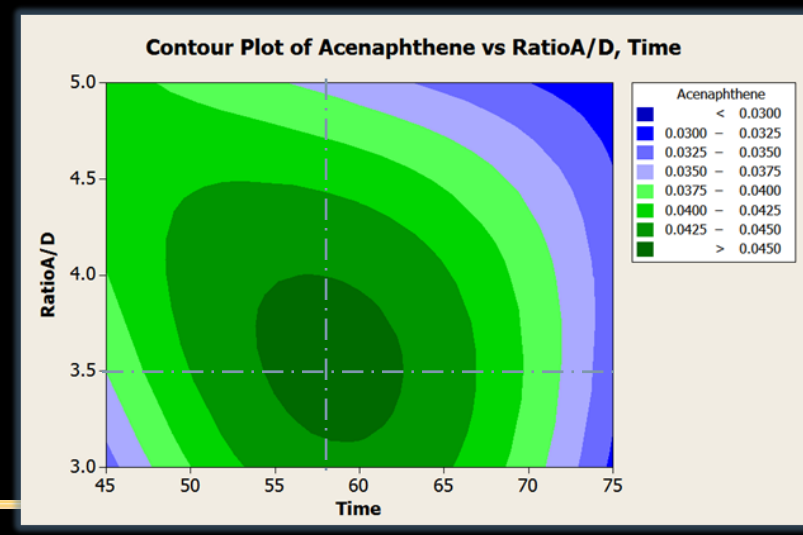
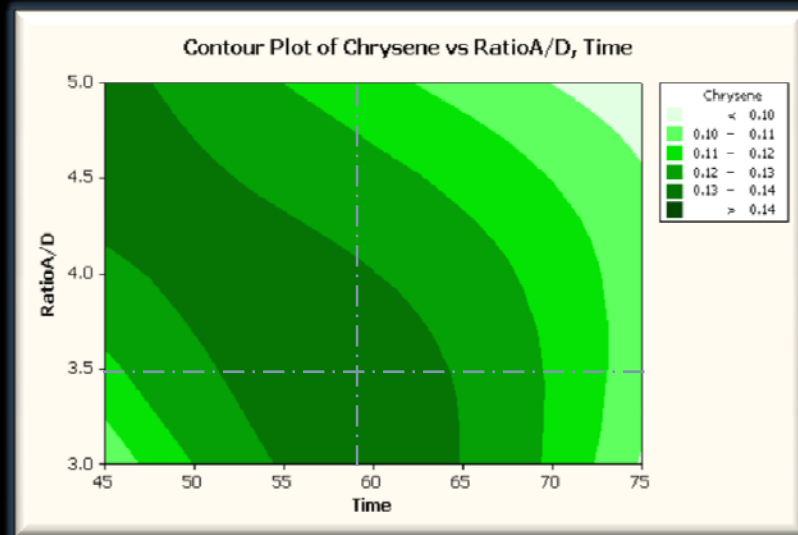
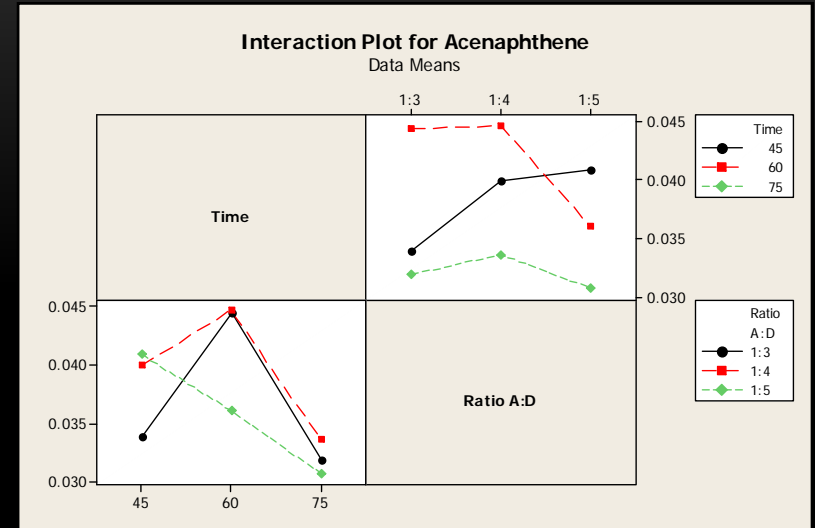
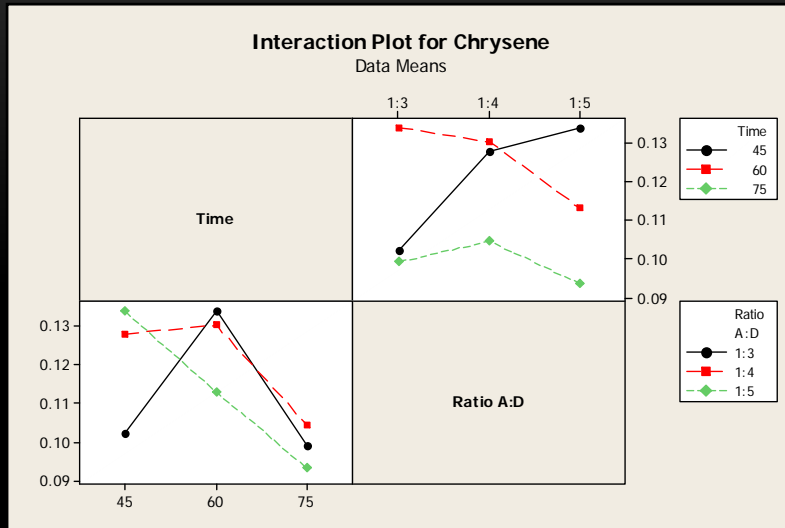


Fig. recovery Interaction plot RatioA/D vs Time for Chrysene – HMW

Fig. recovery Interaction plot RatioA/D vs Time for Acenaphthene - LMW

MODEL ADEQUACY CHECKING

$$e_{ijk} = y_{ijk} - \bar{y}_{ij}$$

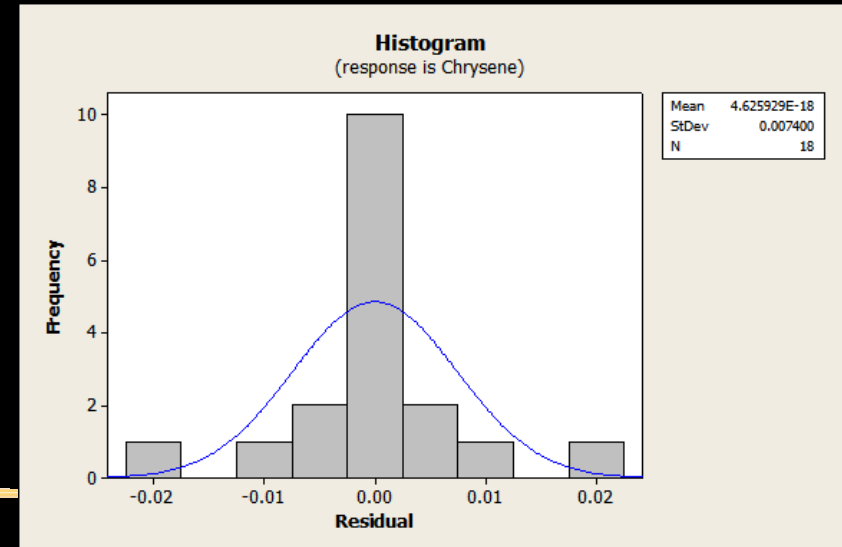
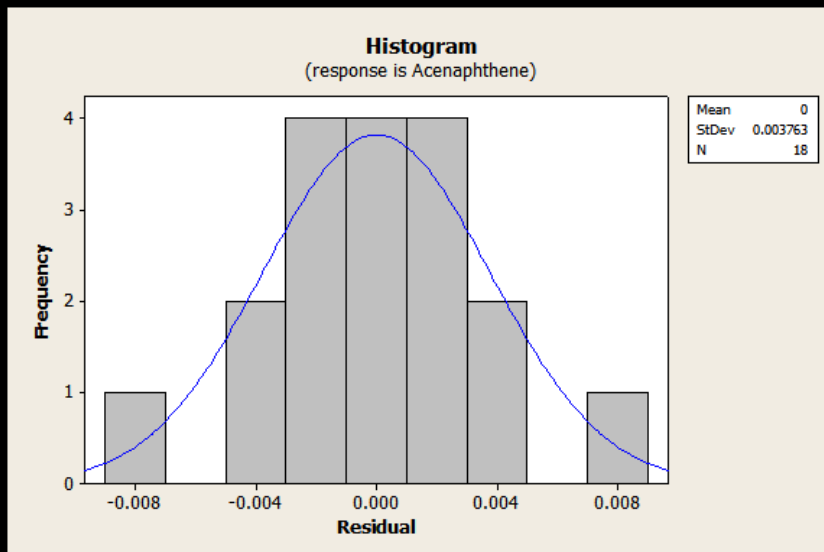
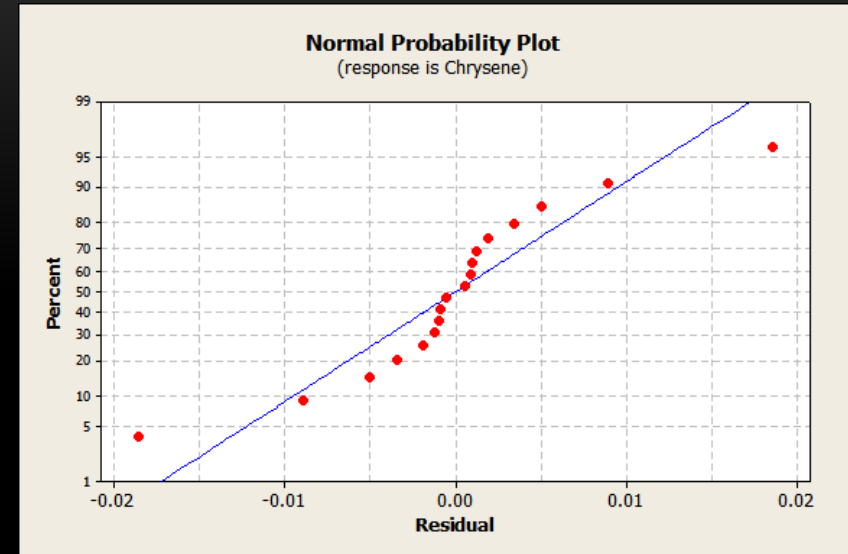
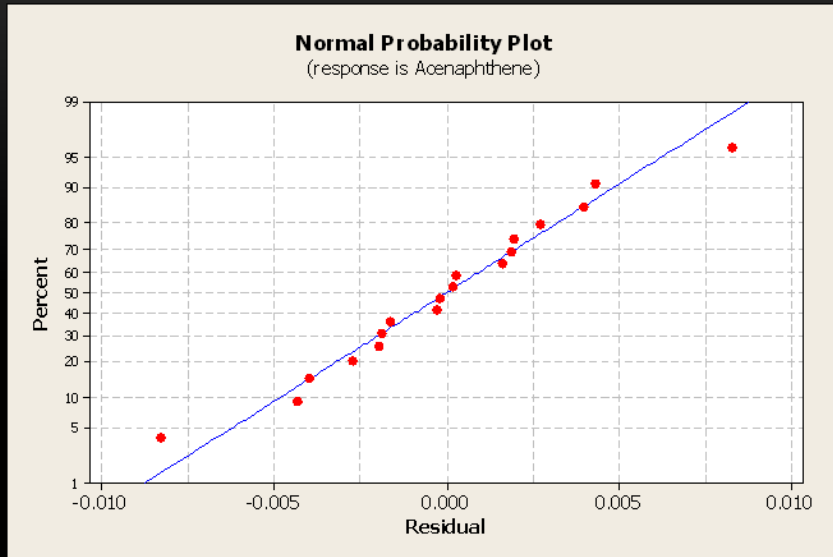


Fig. Normal probability plot and histogram of residuals for Chrysene

Fig. Normal probability plot and histogram of residuals for Acepnahtene

EFFECTIVENESS OF THE CHOSEN COMBINATION

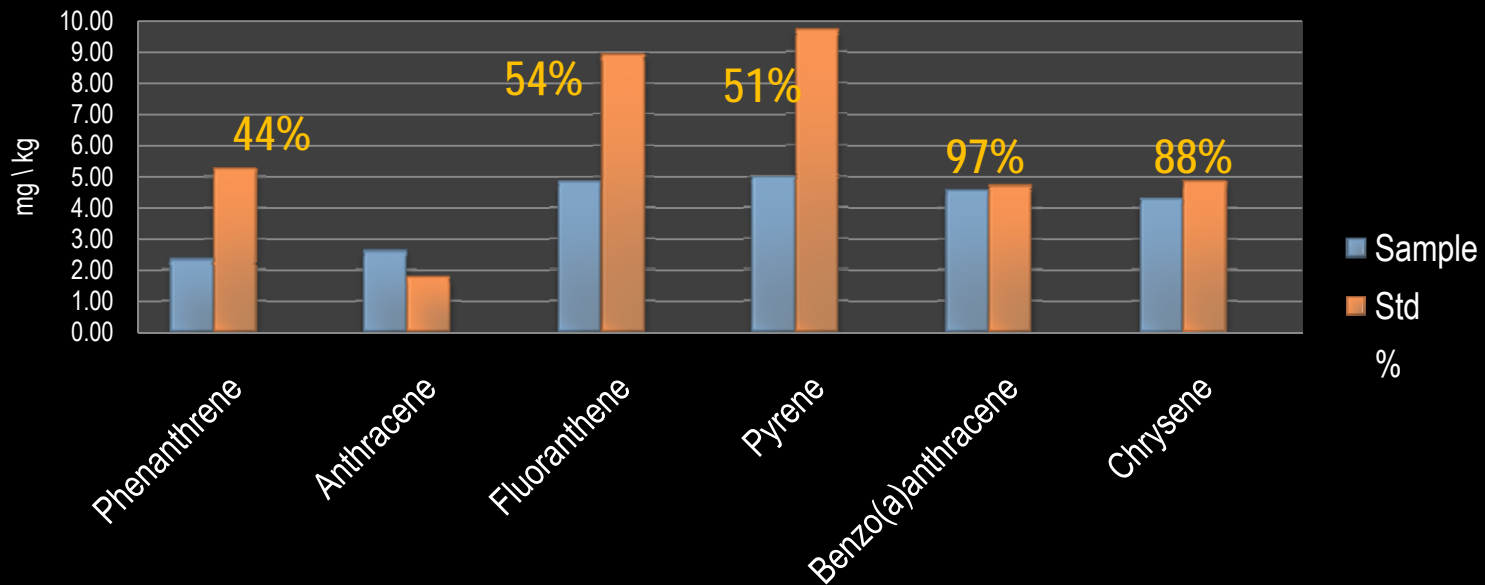
Compound	Concentration (mg/kg)
Phenanthrene	2.34
Fluoranthene	4.83
Pyrene	4.97
Benzo(a)anthracene	4.59
Chrysene	4.29

1:4 Ratio / 60 min (Average)

Compound	Concentration Std (mean) mg/kg
Phenanthrene	5.27
Fluoranthene	8.92
Pyrene	9.70
Benzo(a)anthracene	4.72
Chrysene	4.86

Standard Sample NIST- SRM 1944

Average percentage recovery



MAIN CONCLUSIONS

- There is an “ optimum” combinations under the current experiment conditions and type of samples. This combination was sonication for 60 min and the ratio A/D 1:4.
 - There is a statistically significant influence of the time for both Light and heavier compounds.
 - There is evidence of interaction between time and the ratio A/D for the heavy molecular weight compounds.
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RECOMMENDATIONS

- Grain size characterization and its to PAHs recovery.
 - Validation with different types of soils.
 - Influence of the sample moisture
 - Sonication temperature
 - Investigate the primary source if PAH in BMP soils.
 - Expand ratios and type of solvents
 - Increase number of replicates
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