TICs by State-of-the-Art Solid Phase Extraction: Mining the Preliminary Results

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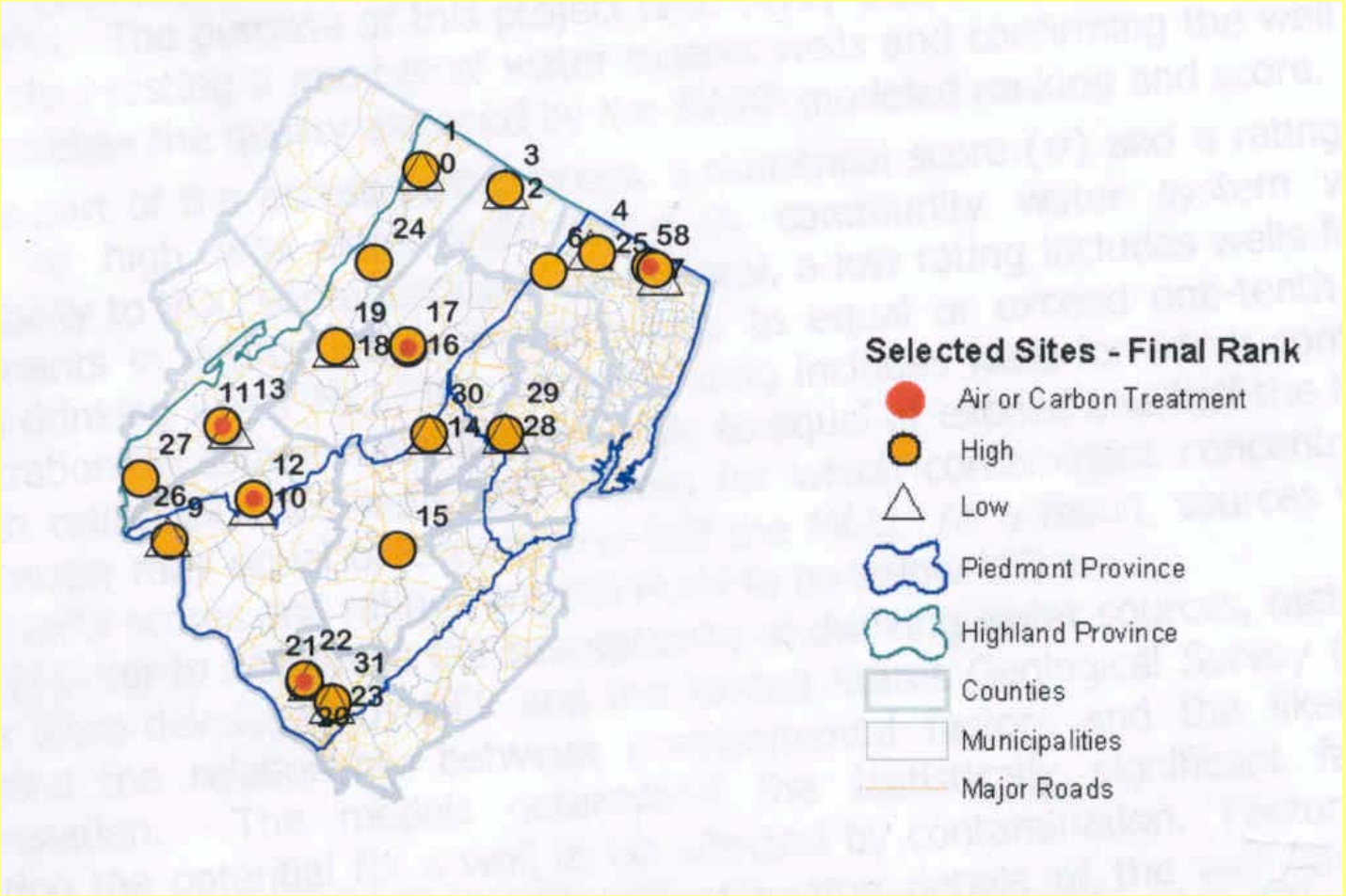
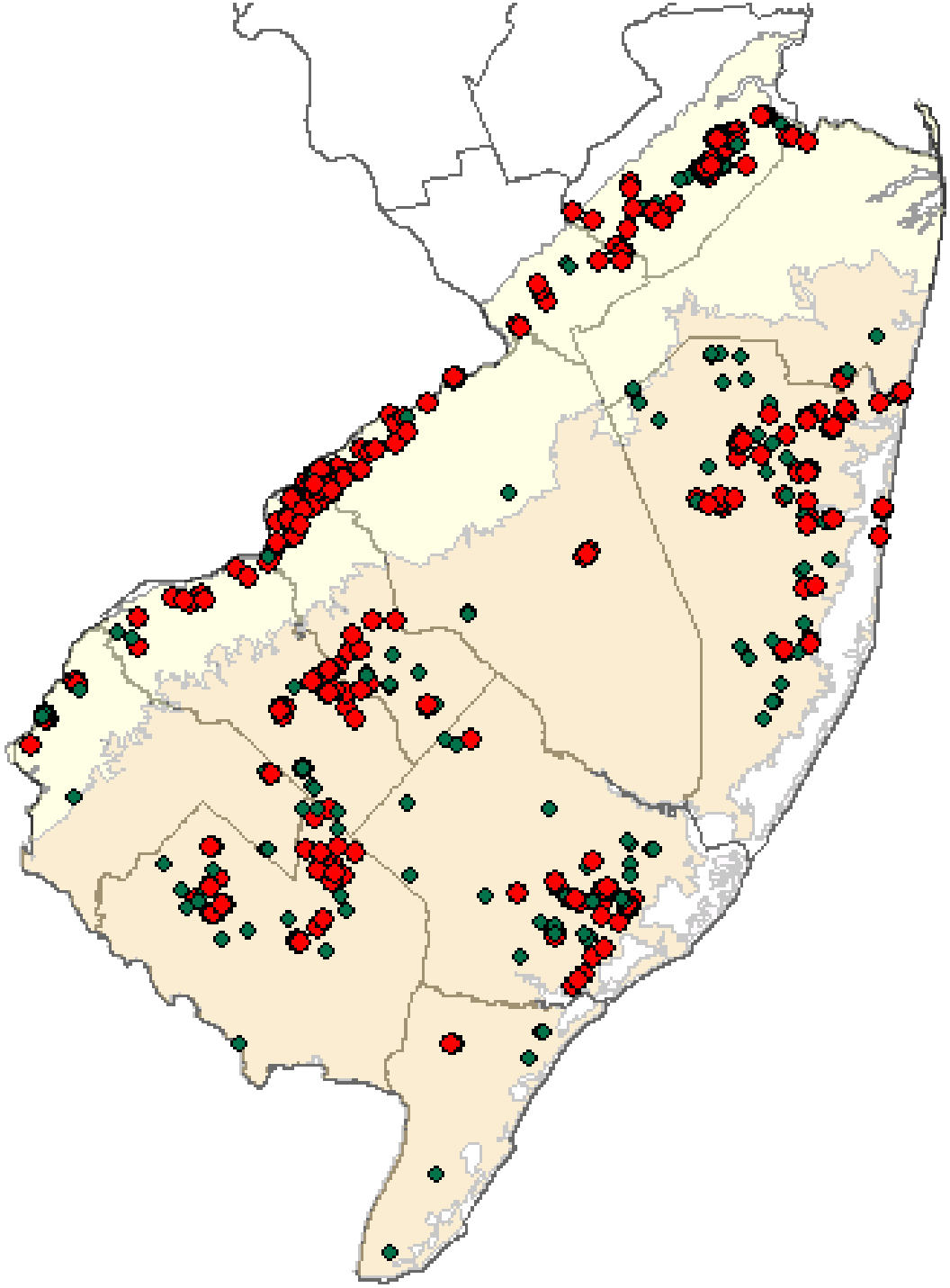
Robert Stiles, Brian Buckley Ph.D.

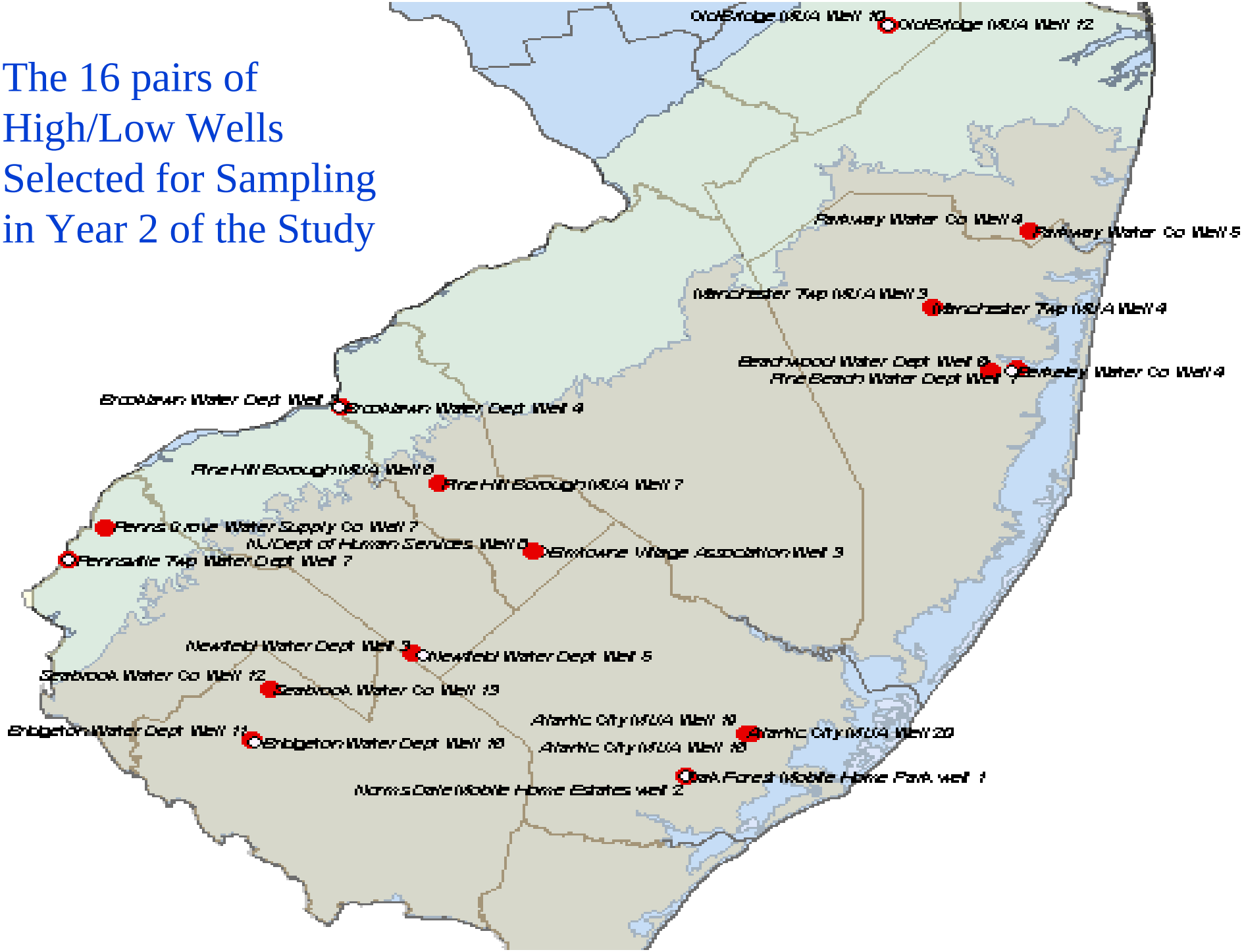
Field Study: Sites of Thirty-one Wells Sampled



All 593 Public Community Supply Wells in the Coastal Plain, with VOC Susceptibility Scores

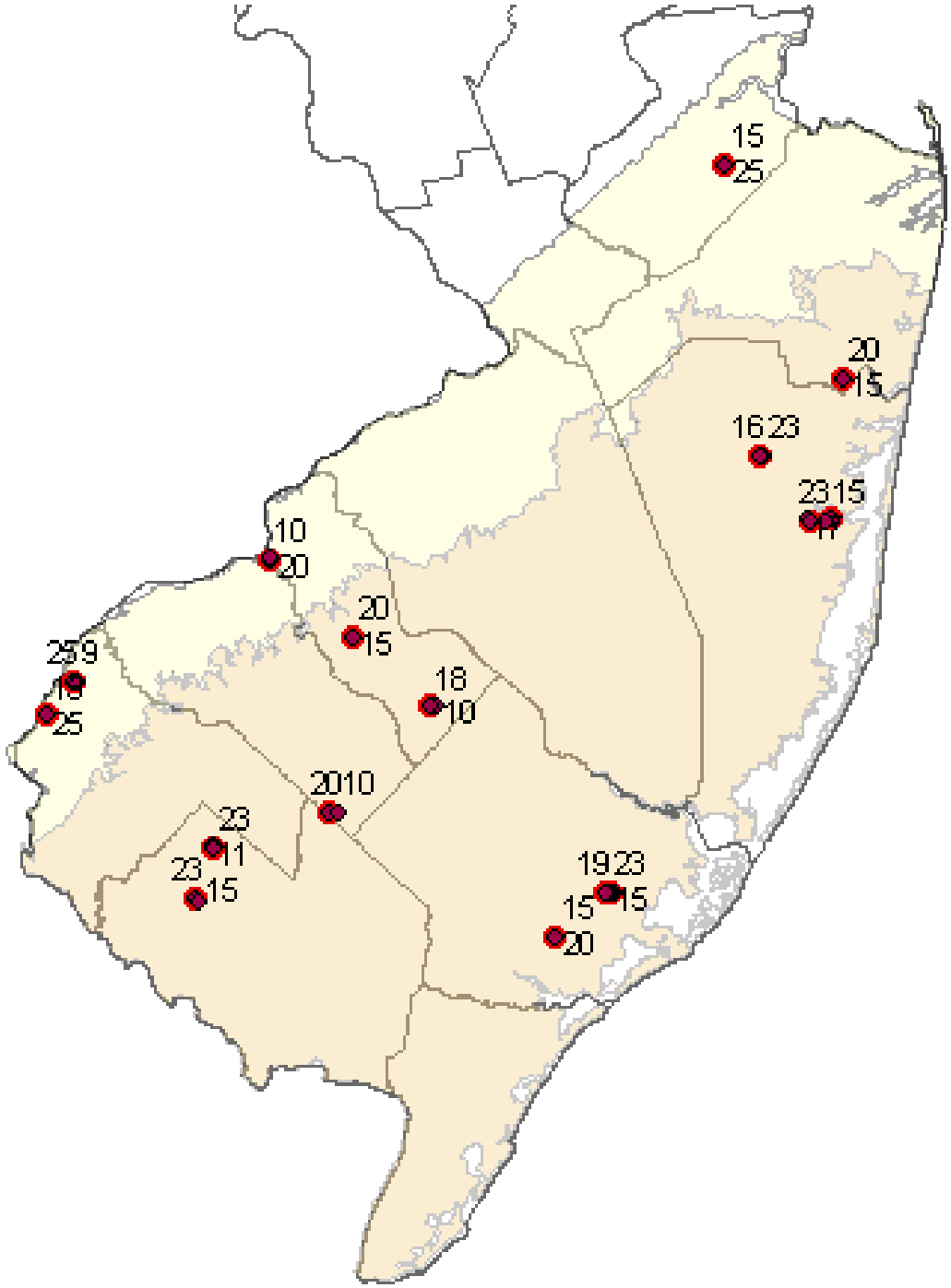


The 16 pairs of High/Low Wells Selected for Sampling in Year 2 of the Study



The 16 High/Low Pairs of Wells Selected for Sampling

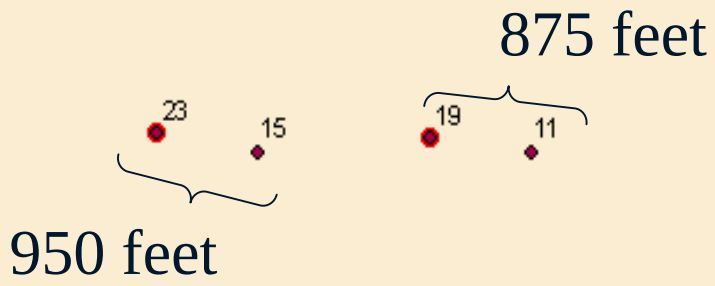
Final Susceptibility Rank shown for each well



Public Community Water Supply Systems in the Coastal Plain with both High and Low Final Susceptibility Ranks

OID	OWNER	Count_OWNER	First_GWFRVOC	Last_GWFRVOC
2	Brooklawn Water Dept	3	High	Low
4	Burlington Twp Water Dept	2	High	Low
10	East Windsor MUA	5	High	Low
11	Elizabethtown Water Co	6	High	Low
23	Old Bridge MUA	10	High	Low
25	Penns Grove Water Supply Co	9	High	Low
26	Pennsville Twp Water Dept	6	High	Low
27	Perth Amboy Municipal Utilities	6	High	Low
32	Spotswood Water Dept	4	High	Low

An example of 2 pairs of High/Low Wells



Field	Value
WPERMIT	31-52209
OWNER	Pine Hill Borough MUA
SYSTEM	
WELLNAME	Well 7
WELLADD	Turnersville Rd & Estate Rd
COUNTY	Camden
MUNICIPALI	Pine Hill Boro
QUAD_NAME	Clementon NJ
EAST	355822.82
NORTH	344482.77
COMPDATE	10/29/1997
TDEPTH	115
FDEPTH	115
SELEV	150
CASDIAL	10
TOPOI	60
BOTOI	110
SCRDIA	10
SWL	7.1
DRILLER	Uni-Tech Drilling Co Inc
DRILLING_M	Rotary (unspecified)
GEONAME	Cohansey & Kirkwood Formations
HYDRONAME	Kirkwood-Cohansey water-table aquifer system
CONFINEMEN	Unconfined
PUMPRATE	0
WTRSHED	Great Egg Harbor and Tuckahoe
PRVNCE	Coastal Plain
GEOLOG	No
LITHOLOG	Yes
OID_	2071
COUNTY_1	Camden
CONSTAT	Unconfined
WELL_NO	3152209
P_IMPSURF_	5
P_COMM_IND	0
URBAN_SQMI	5
DENBINS15_	5
OM_R_SCORE	5
GW_VOC_INT	15
VOC_INTENS	High
GW_VOC_SEN	5
VOC_SENSIT	High
GW_VOC_SUS	20
VOC_SUSCEP	High

Field	Value
WPERMIT	31-49837
OWNER	Pine Hill Borough MUA
SYSTEM	
WELLNAME	Well 6
WELLADD	Turnersville Rd
COUNTY	Camden
MUNICIPALI	Pine Hill Boro
QUAD_NAME	Clementon NJ
EAST	356263.2
NORTH	344260.8
COMPDATE	09/18/1995
TDEPTH	126
FDEPTH	90
SELEV	148
CASDIAL	10
TOPOI	70
BOTOI	90
SCRDIA	10
SWL	7.2
DRILLER	AC Schultes & Sons Inc
DRILLING_M	Rotary (unspecified)
GEONAME	Cohansey & Kirkwood Formations
HYDRONAME	Kirkwood-Cohansey water-table aquifer system
CONFINEMEN	Unconfined
PUMPRATE	0
WTRSHED	Great Egg Harbor and Tuckahoe
PRVNCE	Coastal Plain
GEOLOG	No
LITHOLOG	No
OID_	2067
COUNTY_1	Camden
CONSTAT	Unconfined
WELL_NO	3149837
P_IMPSURF_	5
P_COMM_IND	0
URBAN_SQMI	0
DENBINS15_	5
OM_R_SCORE	5
GW_VOC_INT	10
VOC_INTENS	Low
GW_VOC_SEN	5
VOC_SENSIT	High
GW_VOC_SUS	15
VOC_SUSCEP	Low

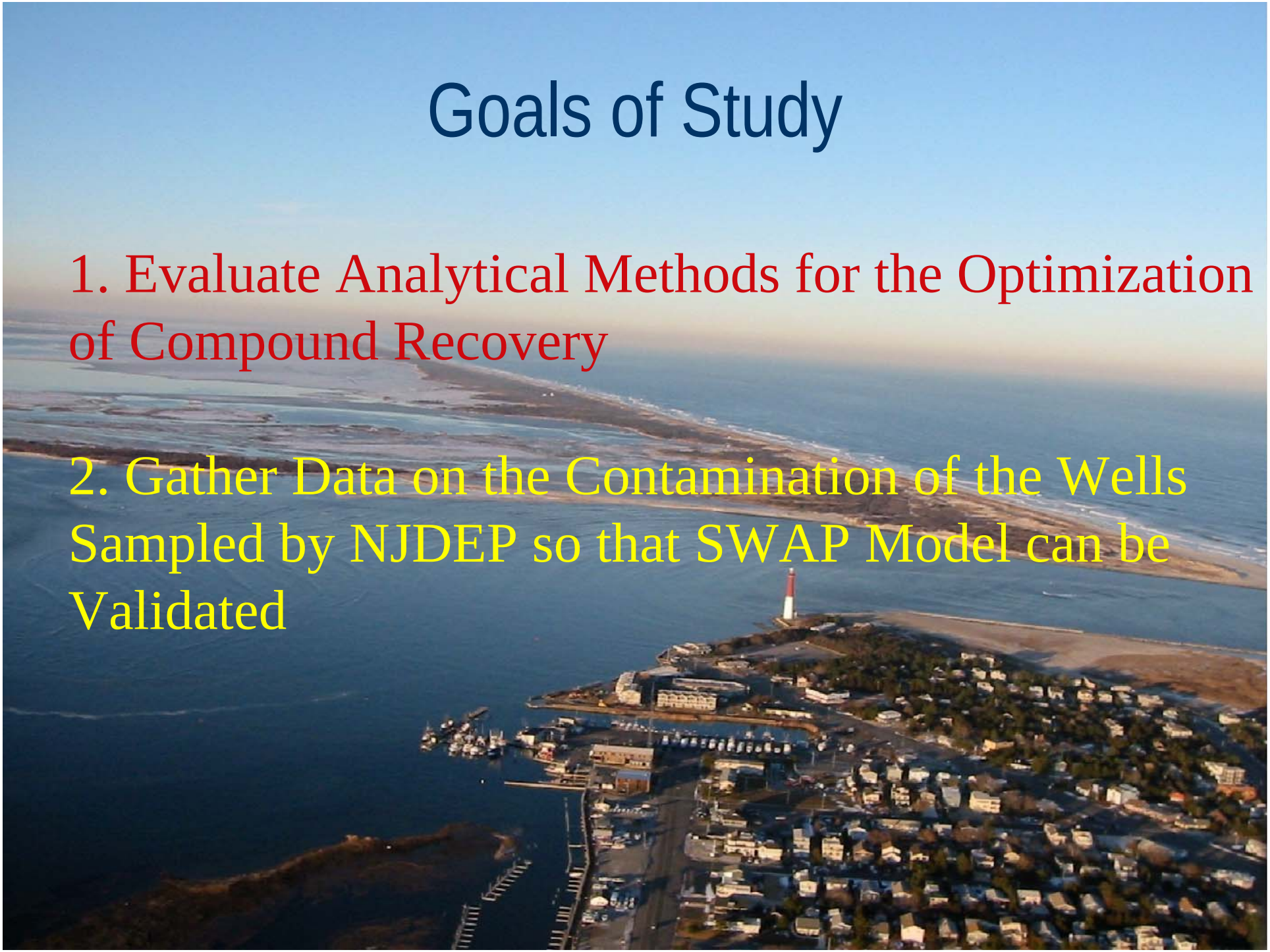
NJDEP Source Water Assessment Program (SWAP)

- Model Developed by NJDEP and USGS Relating Groundwater Quality to Land Use Patterns
- 2337 Community Water Supply Wells in New Jersey
- Wells Given a Score and Rating Based on Sensitivity and Intensity of Use Factors

Goals of Study

1. Evaluate Analytical Methods for the Optimization of Compound Recovery

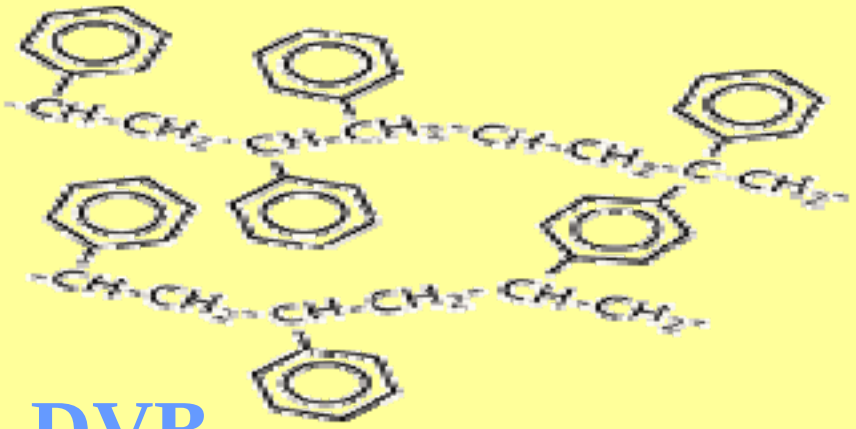
2. Gather Data on the Contamination of the Wells Sampled by NJDEP so that SWAP Model can be Validated



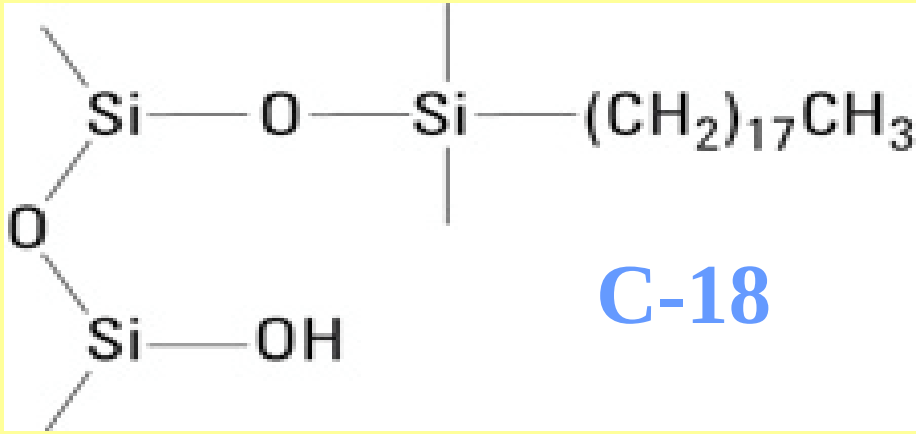
Previous Work

- EPA 8270 and 525.2 Analyzes Water for Semi volatile Organic Contaminants (SVOCs) by SPE-GC/ITMS
- Method Detection Limits (MDLs) Lowered for PAHs, PCBs and Pesticides using Modified EPA 525.2 Method
- Field Tested Method on Water Treatment Plants in New Jersey
- Detection of a Number of Unregulated Contaminants

Solid Phase Materials

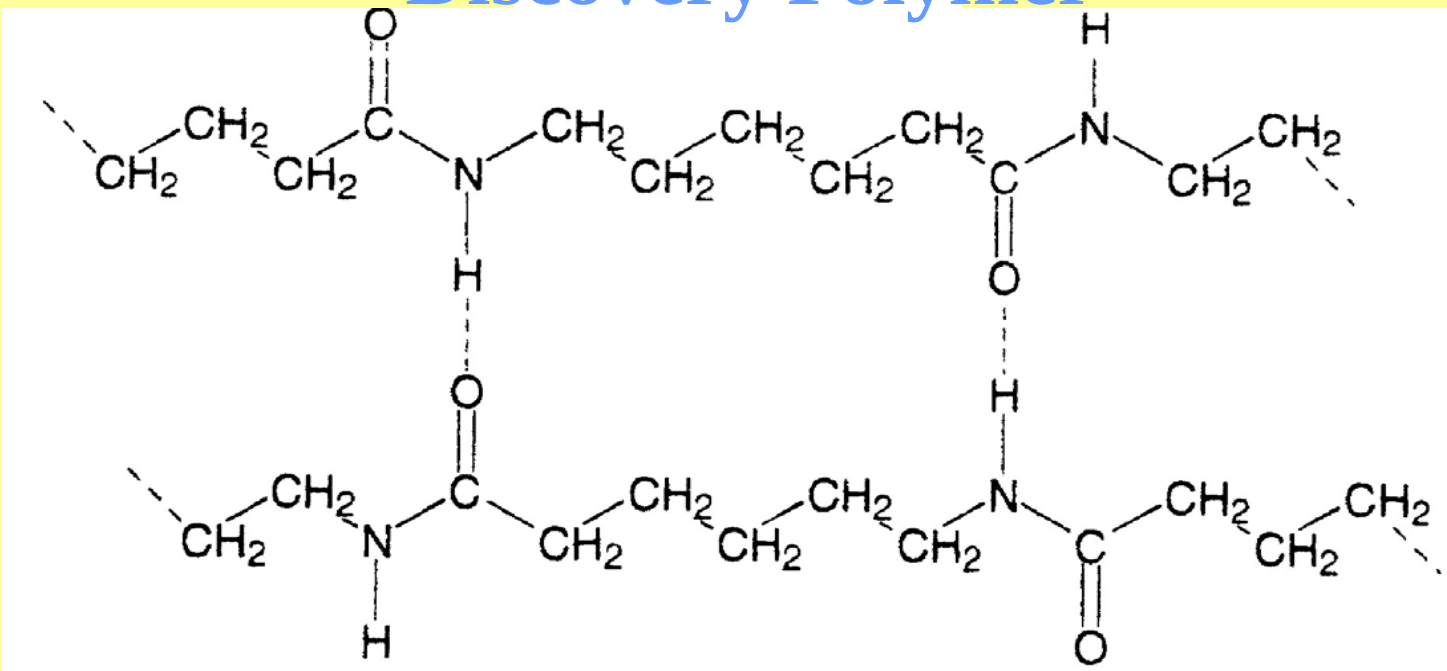


DVB

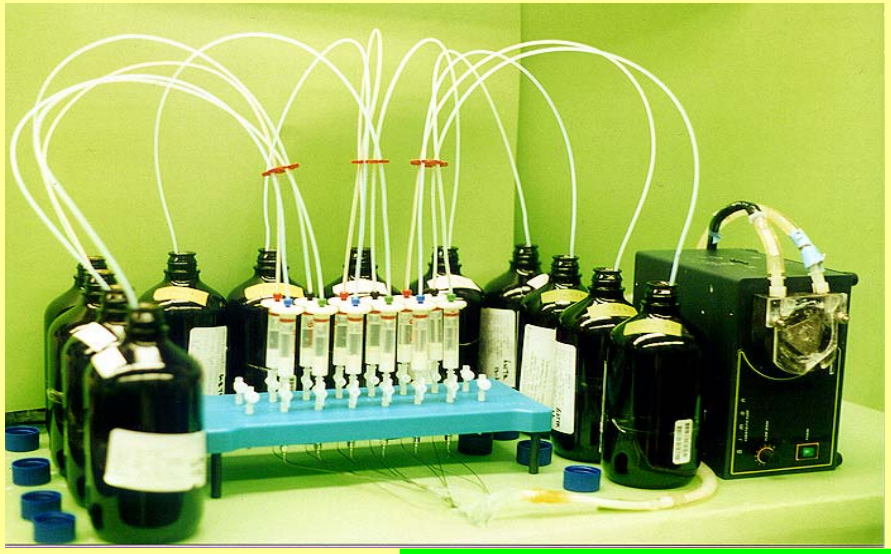


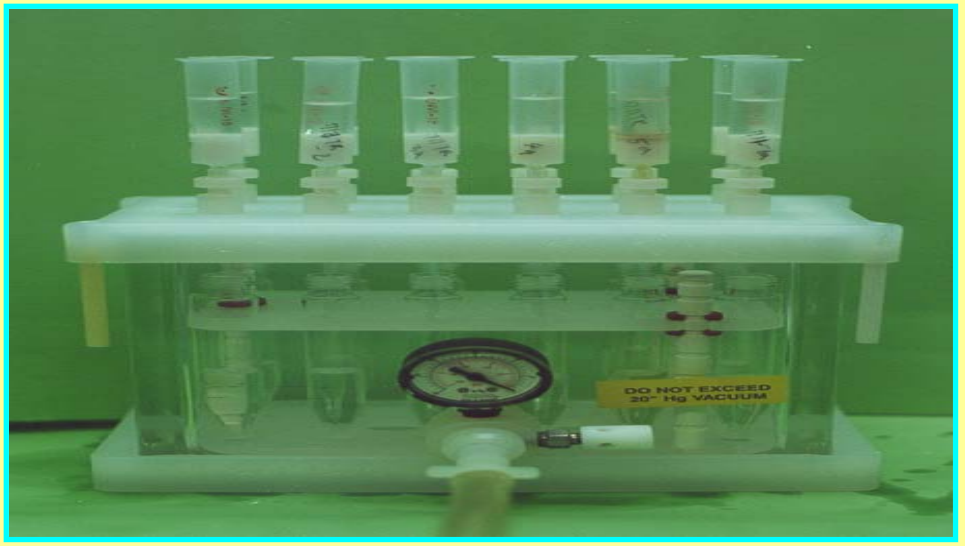
C-18

Discovery Polymer

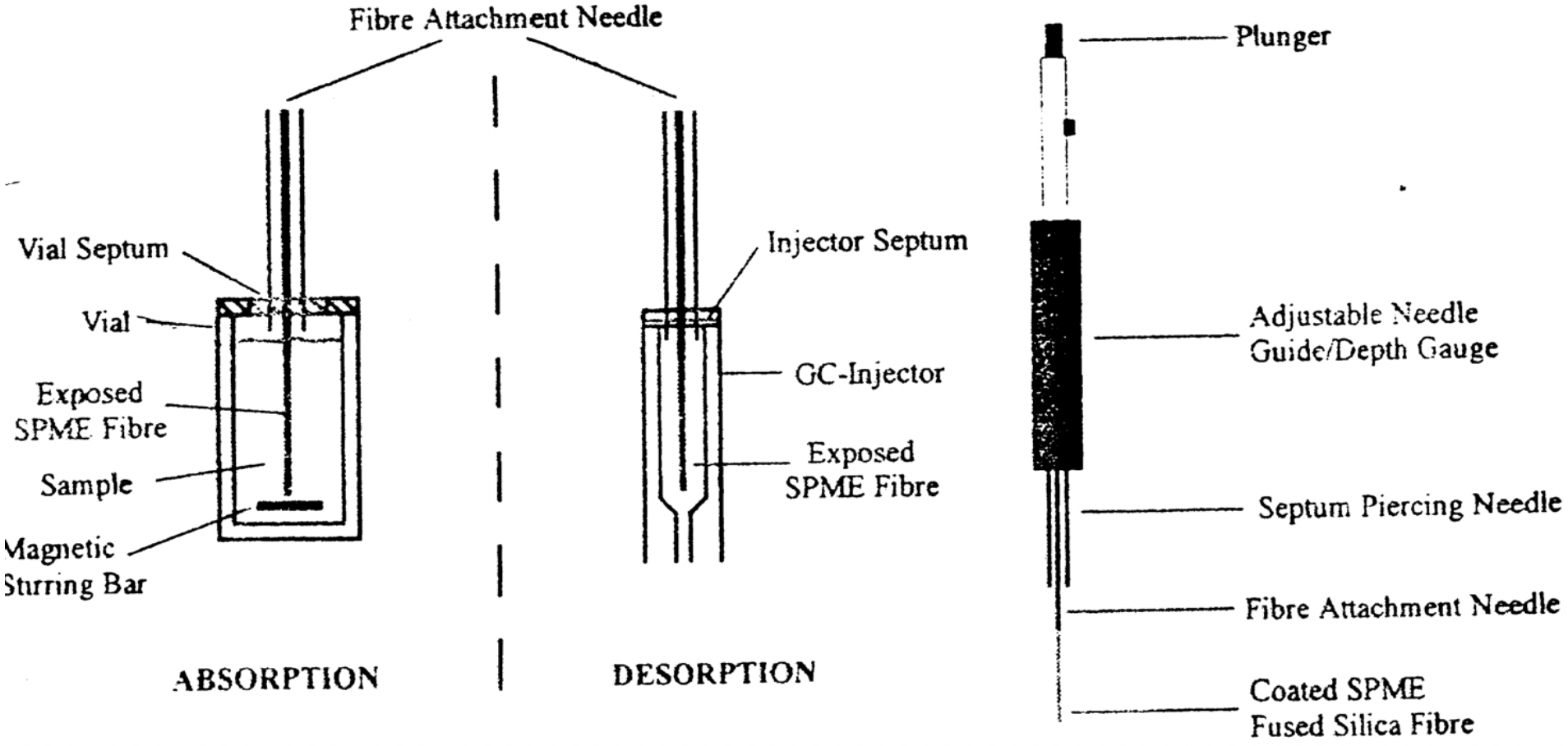


Analytical Instrumentation





Solid Phase Microextraction (SPME)

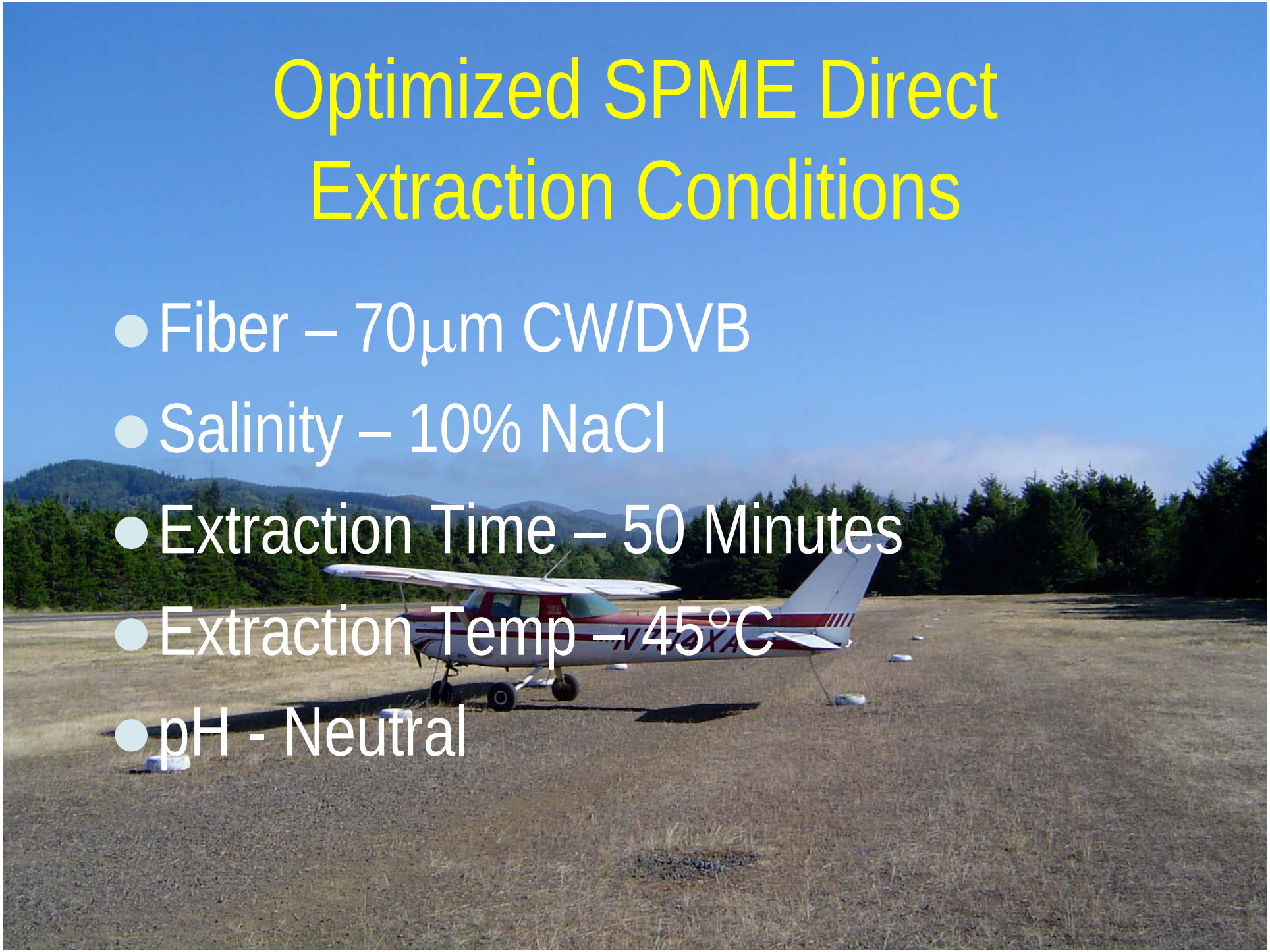


J. Chromatography A, **1996**, *733*, 143-157

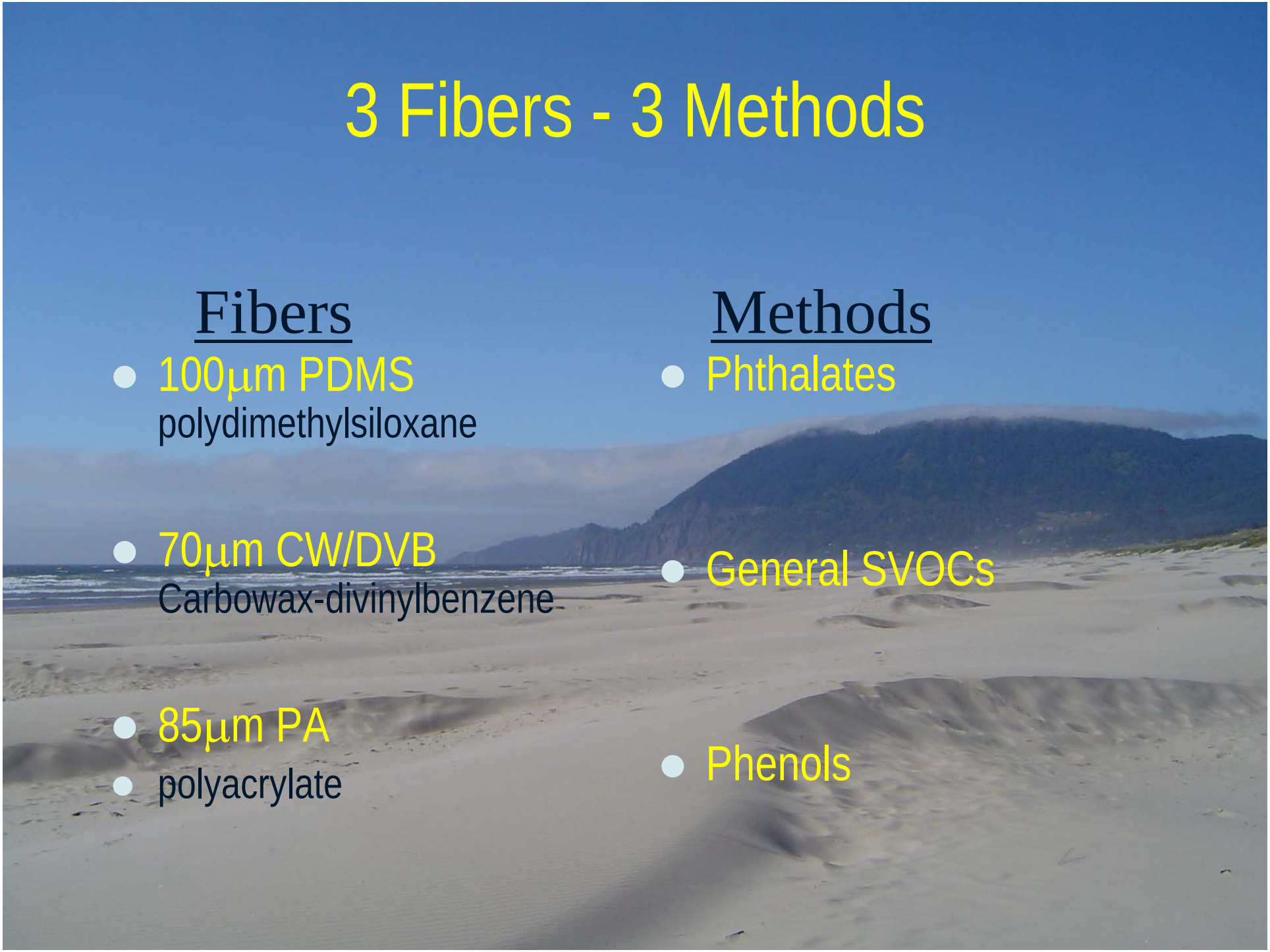
Parameters to Optimize for SPME

- Fiber
- Agitation
- Salinity
- Extraction Time
- Extraction Temperature
- pH
- Sampling Mode

Optimized SPME Direct Extraction Conditions



- Fiber – 70μm CW/DVB
- Salinity – 10% NaCl
- Extraction Time – 50 Minutes
- Extraction Temp – 45°C
- pH - Neutral



3 Fibers - 3 Methods

Fibers

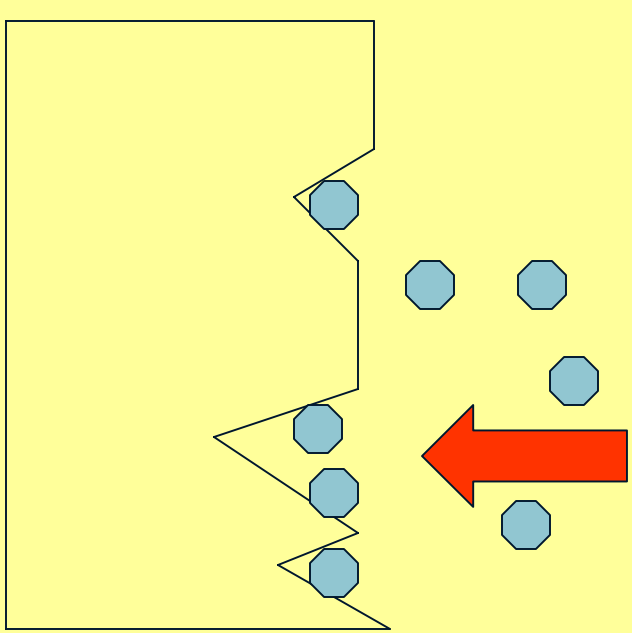
- 100μm PDMS
  polydimethylsiloxane
- 70μm CW/DVB
  Carbowax-divinylbenzene
- 85μm PA
- polyacrylate

Methods

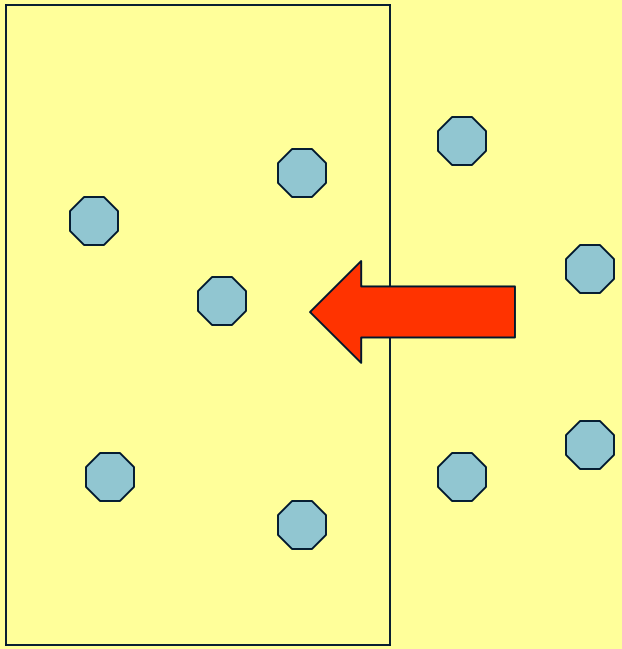
- Phthalates
- General SVOCs
- Phenols

Absorption Vs. Adsorption

Adsorption: Surface Phenomena



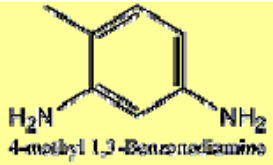
SPME Fiber



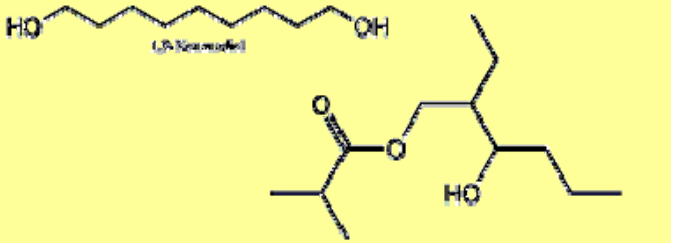
SPME Fiber

Absorption: Diffusion Phenomena

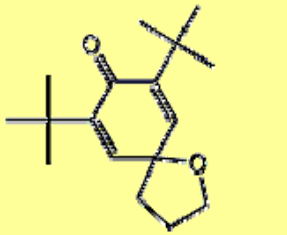
Criteria for Selecting an Extraction Method (SPE vs. SPME)

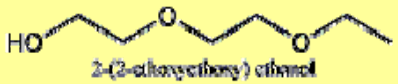


4-methyl 1,3-Benzenediamine

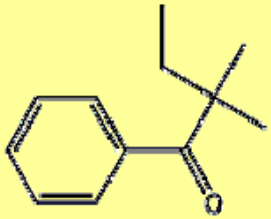


Propanoic Acid, 2-methyl, 2-ethyl-3-hydroxyhexyl ester

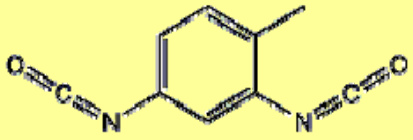




2-(2-ethoxyethoxy) ethanol

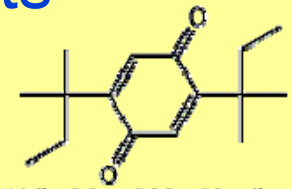


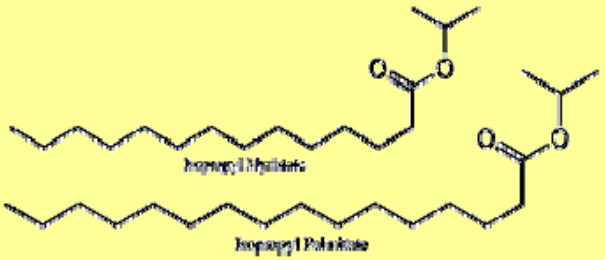
trimethylpropiophenone

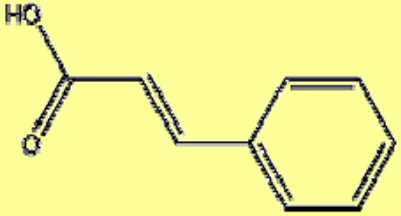


2,4-diisocyanato-1-methyl Benzene

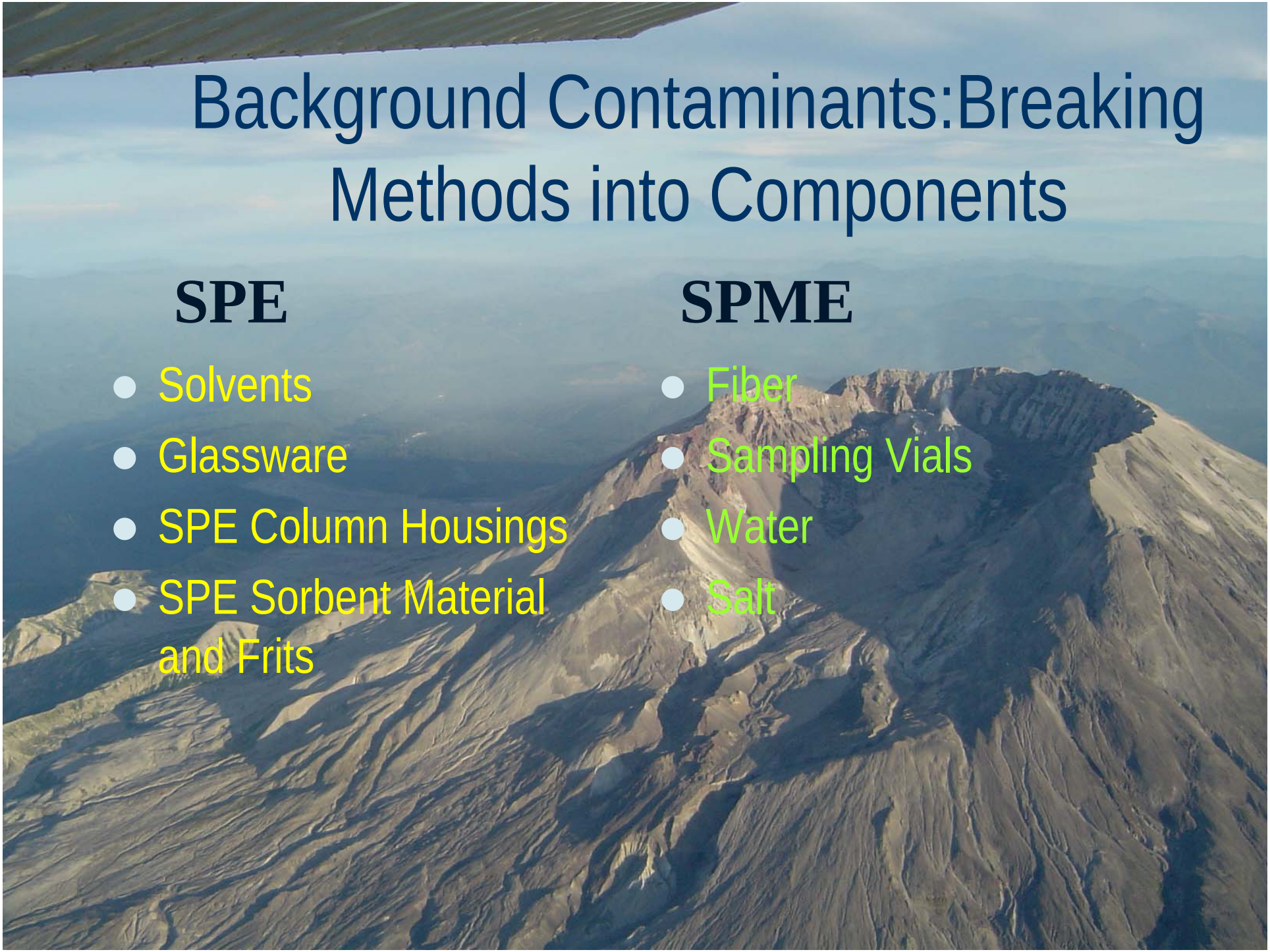
- Cost/Time of Analysis
- Background Contaminants
- Sample Consumption
- Method Detection Limits
- Field Test







2-Propenoic acid, 3-phenyl



Background Contaminants:Breaking Methods into Components

SPE

- Solvents
- Glassware
- SPE Column Housings
- SPE Sorbent Material and Frits

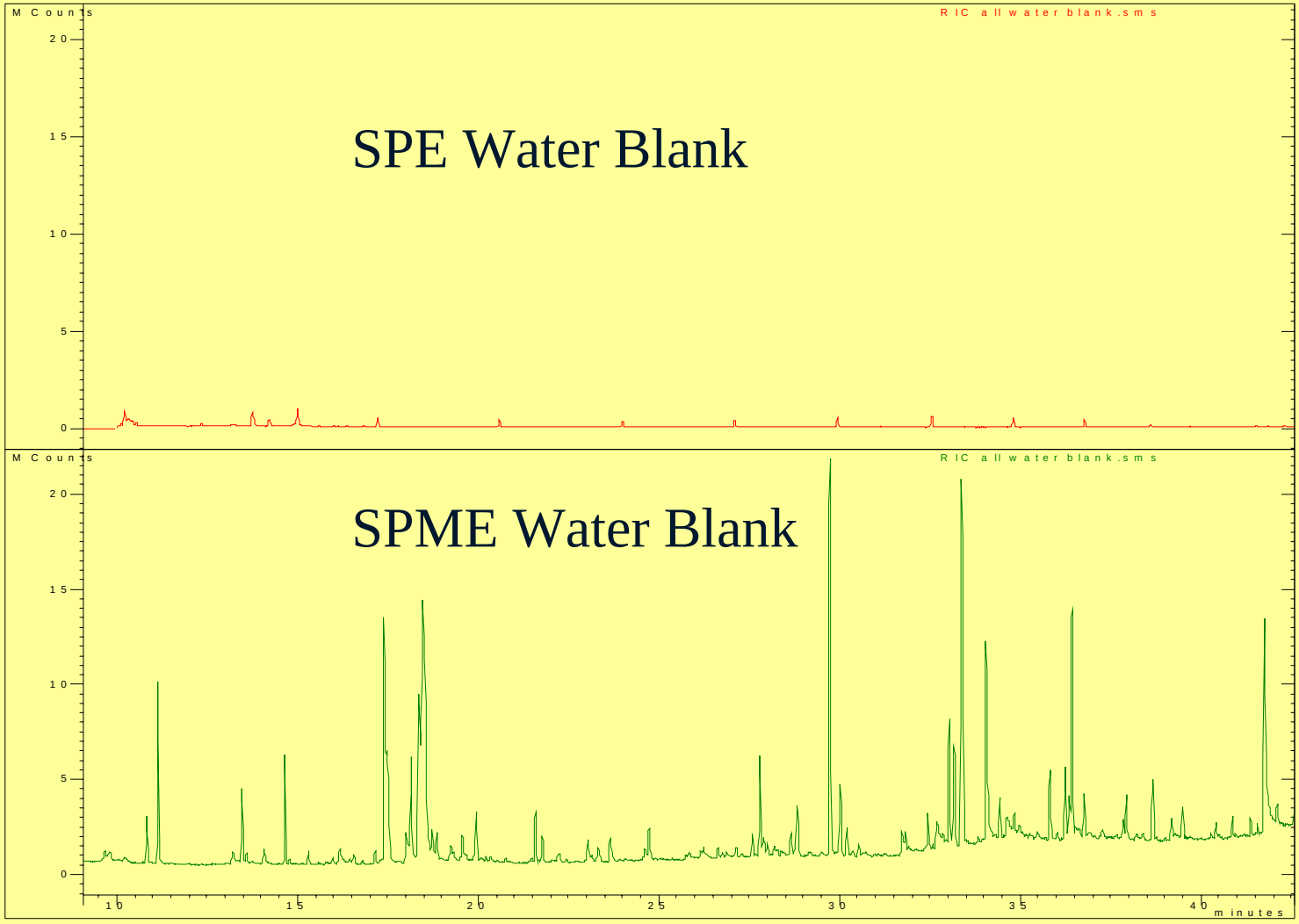
SPME

- Fiber
- Sampling Vials
- Water
- Salt

Most Frequently Detected SPME Artifacts

Compound	Source(s)
1,9-Nonanediol	Carbowax Phase of SPME Fiber
Bis Substituted Compounds	Epoxy Glue of SPME Needle
Cyclodecanol	SPME Vial or Crimp Top
Dibutyl Phthalate	SPME Vial or Crimp Top
Isopropyl Myristate	SPME Vial or Crimp Top (Leached by Water)
Isopropyl Palmitate	SPME Vial or Crimp Top (Leached by Water
(Z)-. 6,10-dimethyl-5,9-Undecadien-2-one	SPME Vial or Crimp Top

Relative Intensity of Blanks



Background Contaminants (Summary)

- SPE – Artifacts are Mostly Plasticizers Originating from Sorbent Material and Frits
- SPME – Artifacts have a Wide Range of Sources and are Fiber Dependent
- SPE has a Greater Number of Artifacts but in Lower Concentrations

Method Detection Limits: SPME vs. USGS

	CW/DVB MDLs (ppb)	USGS RLs (ppb)
bis (2-ethylhexyl) adipate	1.0	2000.0
carbaryl	10.0	60.0
butylated hydroxy toluene	1.0	80.0
bisphenol A	1.0	90.0
N,N-diethyltoluamide	1.0	40.0
dieldrin	0.1	80.0
cis-chlordane	0.1	40.0
lindane	0.1	50.0
tetrachloroethylene	n.d.	30.0
diazinon	1.0	30.0
chlorpyrifos	1.0	20.0
triphenyl phosphate	1.0	100.0
methyl parathion	n.d.	60.0
1,4-dichlorobenzene	0.5	30.0
acetophenone	n.d.	150.0
bis (2-ethylhexyl) phthalate	0.5	2500.0
diethyl phthalate	0.5	250.0
4-methylphenol	0.5	40.0

Environmental Science and Technology, **2002**, *36*, 1202

Number of Unique Analytes Detected in Wells

Compound Class	Direct SPME	SPE
Brominated	35	1
Chlorinated	6	14
Phenols	14	12
Benzenes	11	3
PAHs	5	0
Phthalates	5	3
Alcohols	10	11
Ketones	17	8
Aldehydes	4	1

Future Directions

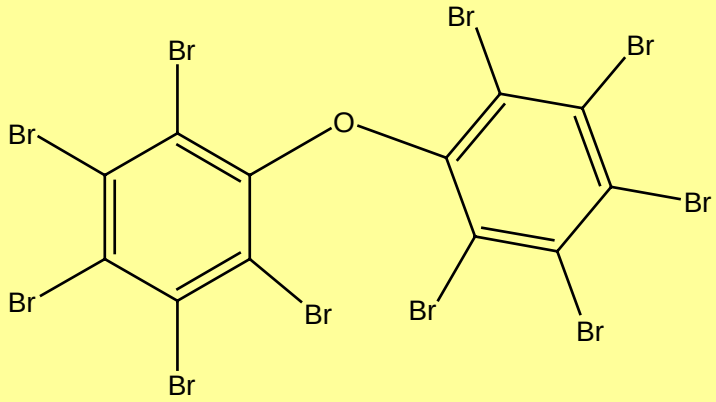
- Field Sampling of Wells In the Coastal Plain
- Development of SPME-LC/MS Method
- Investigation of Fibers that can Extract Analytes with Extremely High or Low Log Kow Values

Data Mining Process

- Evaluate Blank Data for repetitive blank contaminants
- Sort Blank Data and Sample Data sets
- Compare Levels of Method Blank Contamination with Sample Contaminants
- Eliminate Blank Constituents from Sample Preliminary Data

Data Prioritization Process

- Look for recurring contaminants in the wells
- Evaluate the quality of the Mass Spectrometry
- Determine Structure and plausibility of existence in the water column
- Determine if you are observing a weathered or hydrolyzed product of another contaminant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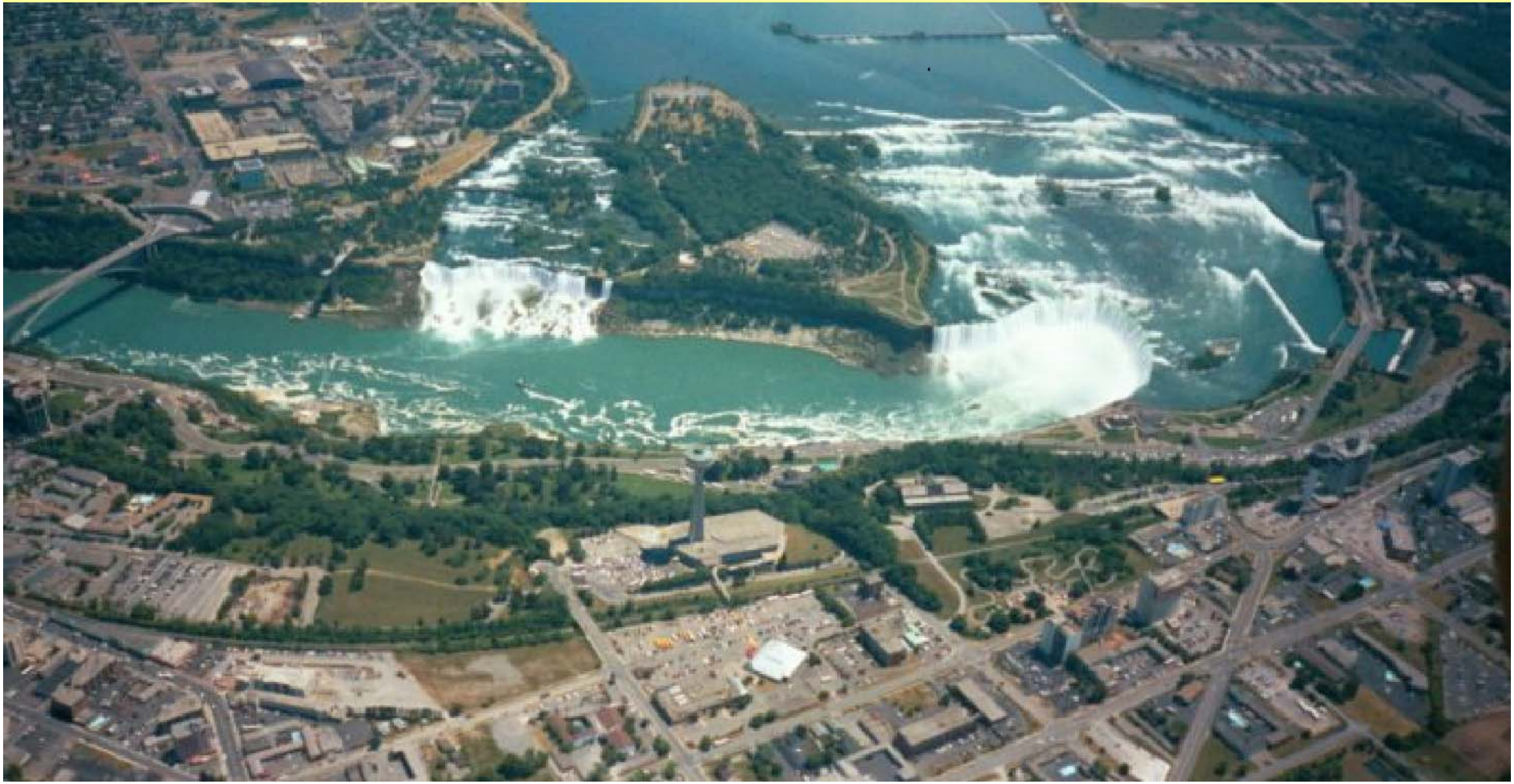
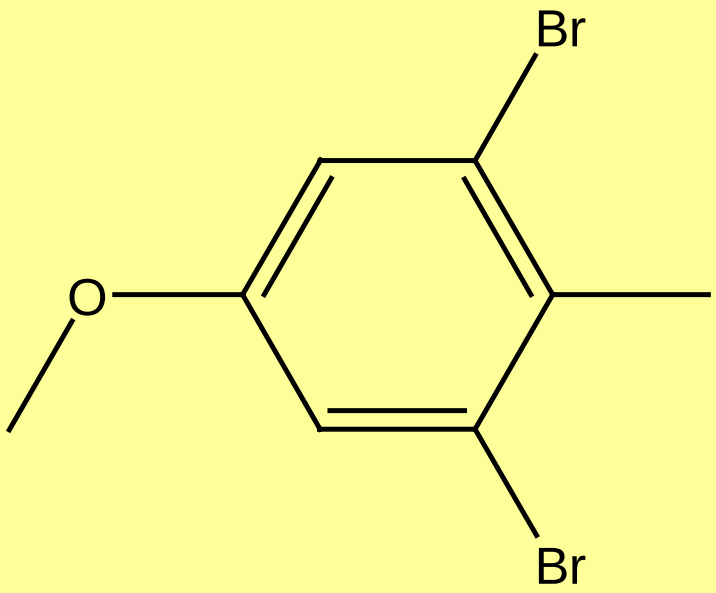
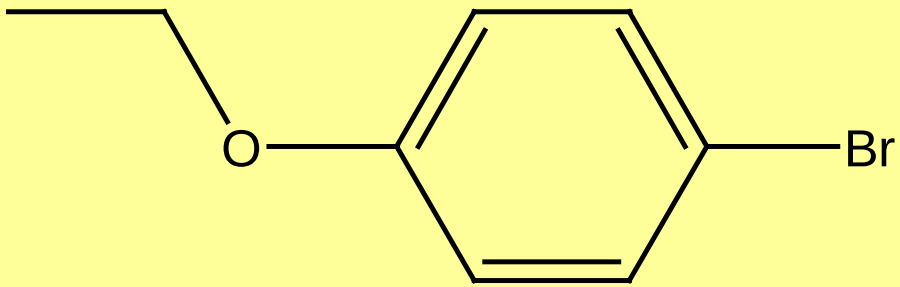


FRAGMENTS OF PBDE's ?

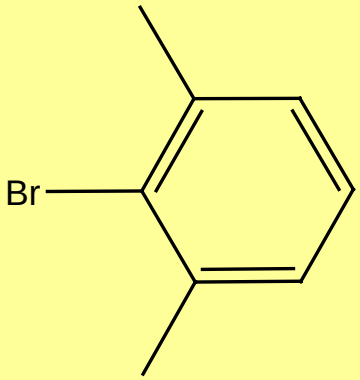


2,6-dibromo-4-methoxytoluene

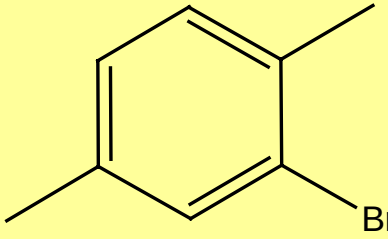


1-bromo-4-ethoxy-benzene

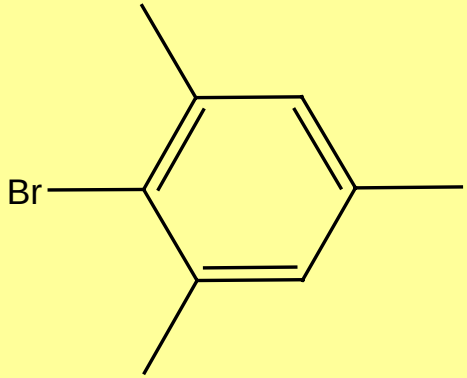
OR BROMINATED DBP's ?



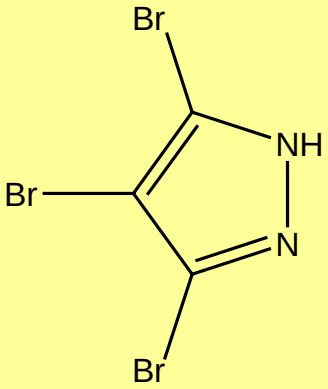
2-bromo-m-xylene



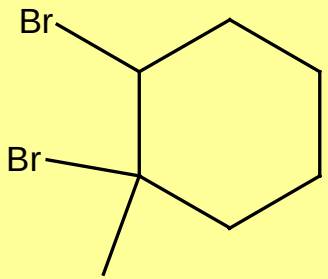
2-bromo-1,4-dimethyl Benzene



2-bromo-1,3,5-trimethylbenzene



3,4,5-tribromo-1H-Pyrazole



1,2-dibromo-1-methyl-cyclohexane

U.S. Environmental Protection Agency
Polybrominated Diphenyl Ethers (PBDEs) Project Plan

March 2006