The Occurrence and Geospatial Distribution of Toxic Organic Contaminants in a Statewide Stratum

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ABSTRACT

In order to protect human health and aquatic ecosystems, the U.S. Environmental Protection Agency has established water quality criteria for numerous toxic organic compounds. These criteria are expressed as four-day water column concentration averages not to be exceeded more than once on average in a three year period. These maximum concentrations are further classified into three categories of protection: 1) public water supplies, 2) aquatic organisms (both acute and chronic effects), and 3) human health by way of consumption of fish tissue. Typically detection of these toxic compounds is from the analysis of sediment and fish tissue and not by direct measurement of water column concentrations. The difficulty to government agencies in making direct measurements of these toxic chemicals is the high cost of analytical methods needed to reach low concentrations and the representativeness as compared to four day averages. The Virginia Department of Environmental Quality (VADEQ) is required by the Federal Clean Water Act and the Virginia Water Quality Monitoring, Information, and Restoration Act to monitor all state waters for all compounds with water quality standards. In order to meet these requirements the VADEQ, for a subclass of these compounds, combined a modified integrative passive sampling device with a probabilistic sampling design (ProbMon). This is the first time that concentrations of trace toxic anthropogenic compounds have been measured on a statewide geospatial scale in free flowing 1st through 5th order and higher streams (n=41). Because of the nature of the stratified random sample design the VADEQ was able to determine the occurrence and distribution of 67 compounds of which 28 have water quality criteria in approximately 50,000 linear stream miles. Selected results are presented on this poster.

What is Virginia's Probabilistic Monitoring Program (ProbMon)?

- ✓ Employs a randomized system for selecting stations
- ✓ Provides statistically based information about water quality in Virginia
- ✓ Includes all non-tidal perennial rivers and streams in Virginia
- ✓ Based on EPA's Environmental Monitoring and Assessment Program (EMAP)

TECHNOLOGY

The following references describe the theory, principle, and application of the use of Semipermeable Membrane Devices (SPMD) used in this project:

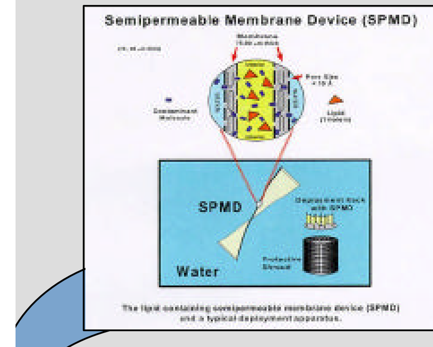
1. Huckins, J.N., Tubergen, M.W., Manuweera, G.K. 1990. Chemosphere 20: 533-553.
2. Huckins, J.N., Manuweera, G.K., Petty, J.D., MacKay, D., Lebo, J.A. 1993. Environ. Sci. Technol. 27: 2489-2496.
3. Lebo, J.A., Gale, R.W., Petty, J.D., Huckins, J.N., Echols, K.R., Schroeder, D.J., Inmon, L.E. 1995. Environ. Sci. Technol., 29: 2886-2892.
4. Petty, J.D., Poulton, B.C., Charbonneau, C.S, Huckins, J.N., Jones, S.B., Cameron, J.T., Prest, H.F. 1998. Environ. Sci. Technol. 32: 837-842.
5. Huckins, J.N., Petty, J.D., Prest, H.F., Clark, R.C., Alvarez, D.A., Orazio, C.E., Lebo, J.A., Cranor, W.L., Johnson, B.T. A Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic Contaminants; Report for the American Petroleum Institute (API); API publication number 4690; API: Washington, DC, 2002.
6. Huckins, J.N., Petty, J.D., Lebo, J.A., Almeida, F.V., Booij, K., Alvarez, D.A., Cranor, W.L., Clark, R.C., Mogensen, B. 2002. Environ. Sci. Technol. 36: 85-91.

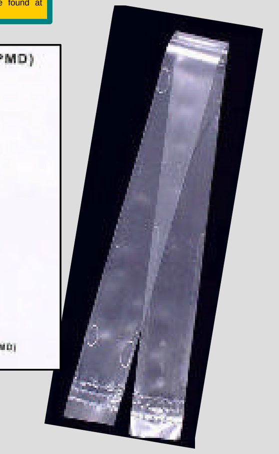
SAMPLE DEPLOYMENT

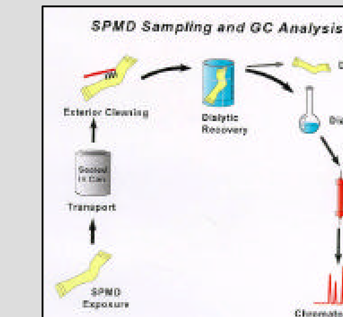
- In expensive disposable sample cages constructed of galvanized hardware cloth were used to house 5 standard SPMD tapes.
- Sample cages were cylindrical being one foot in diameter and 42 inches in length.
- Holes were cut in the loop ends of the tapes to accommodate nylon electrical ties used to secure each tape to the inside end caps of the cages.
- Deployment periods ranged from 30 to 45 days.

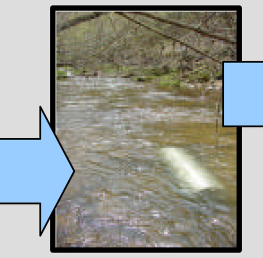
DATA ANALYSIS AND INTERPRETATION

- Chemical analysis was performed by the U.S. Geological Survey, Columbia Environmental Center as described in the references above.
- Probabilistic data analysis: Cumulative distribution function (CDF) produced in this report were generated using the 'R' program. The CDF estimates the probability that a variable is less than or equal to some value. This function is most useful when displayed graphically. Then the viewer is able to determine the likelihood that a variable would be less than a particular threshold. It can also provide the probability that a variable would be above a threshold or that it would be within a certain range. For probabilistic data used in this study, these probabilities apply to all non-tidal streams found in the Commonwealth. Detailed information on CDF curve generation can be found at http://www.epa.gov/nheerl/arm/analysispages/monitanalysisinfo.htm.









APPROACH

The design of this study is modeled after the USEPA EMAP probabilistic program. The target population is all non-tidal perennial streams and rivers within Virginia. The sampling frame is the USEPA RF3 stream reach file, 1:100,000 map scale.

A random tessellation stratified (RTS) survey design[i] was used to select the stream sample sites. Stevens and Olsen[ii] describe the RTS design applied to streams. To ensure sampling would occur in the higher order streams, the sample design was weighted by stream order categories to achieve an approximately equal expected sample size across stream order and across basins.

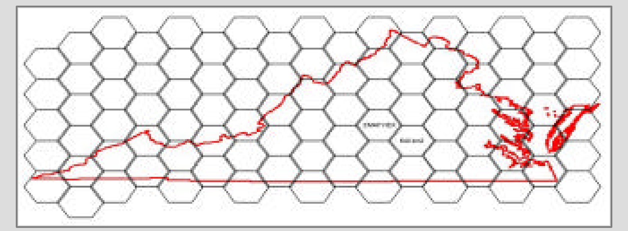
Categories for unequal Probability Selection: The Strahler stream order is used to achieve approximately an equal number of sample sites by 1st, 2nd, 3rd, 4th, and 5th or higher orders each with approximately 12 to 13 sites per year.

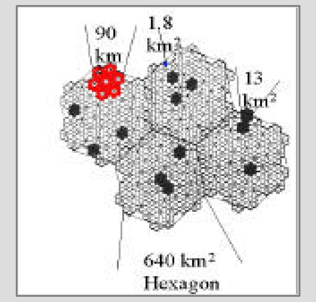
Sub-populations: Over time the sample size will be sufficient to determine the influence of specific sub-populations on water quality. Examples of sub-populations include: water quality classes, eco regions, small watersheds (HUC designations), land use classes, and stream order.

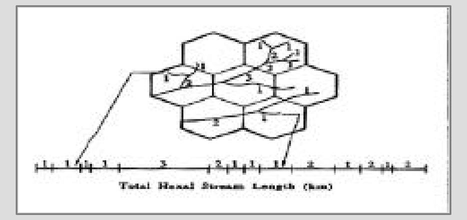
Please see the accompanying map for a graphical representation of station selection process.

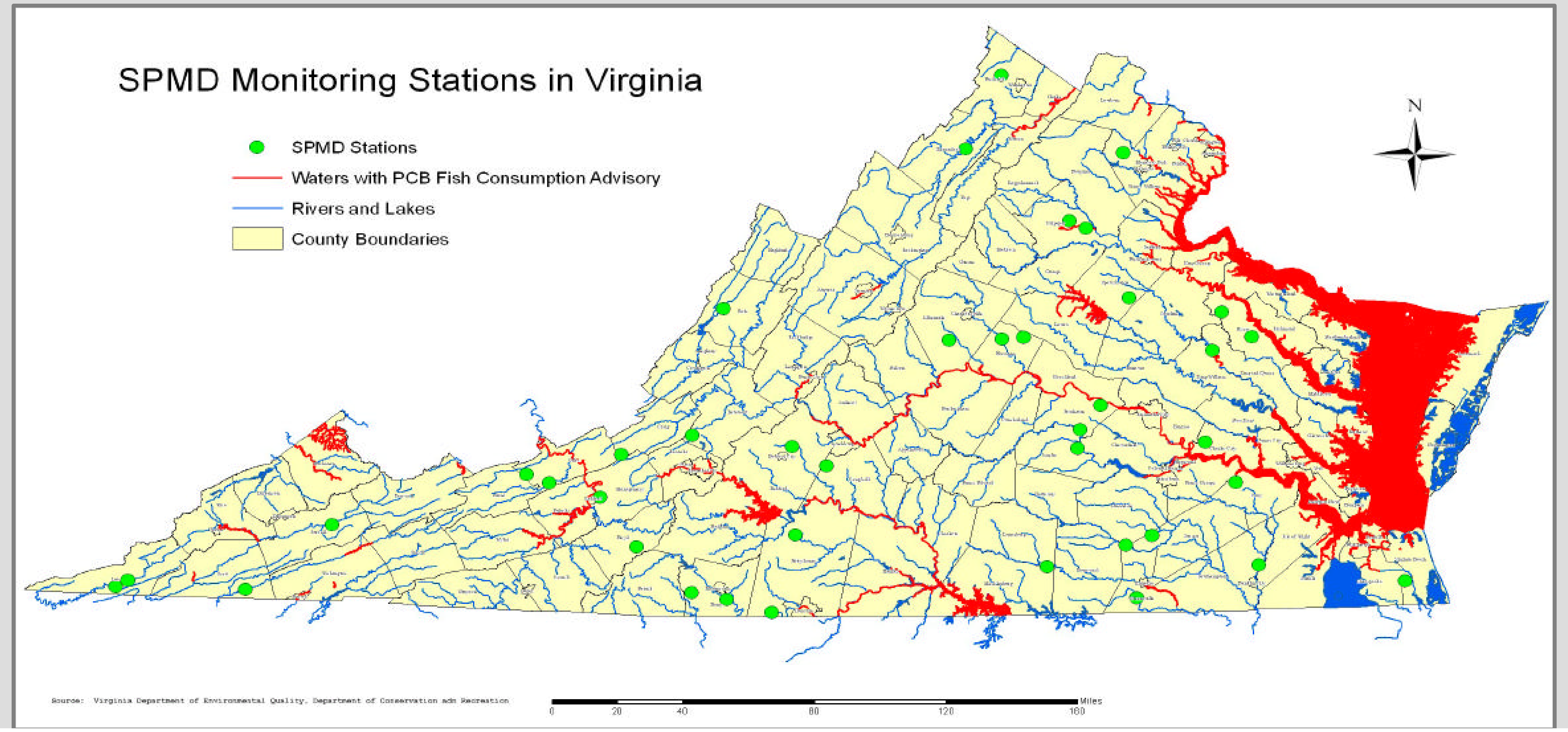
[i] Stevens, D.L., Jr. (1997) Variable density grid-based sampling designs for continuous spatial populations. Environmetrics, 167-95.

[ii] Stevens, D.L., Jr. and Olsen, A.R. (1999) Spatially restricted surveys over time for aquatic resources. Journal of Agricultural, Biological, and Environmental Statistics, (submitted).





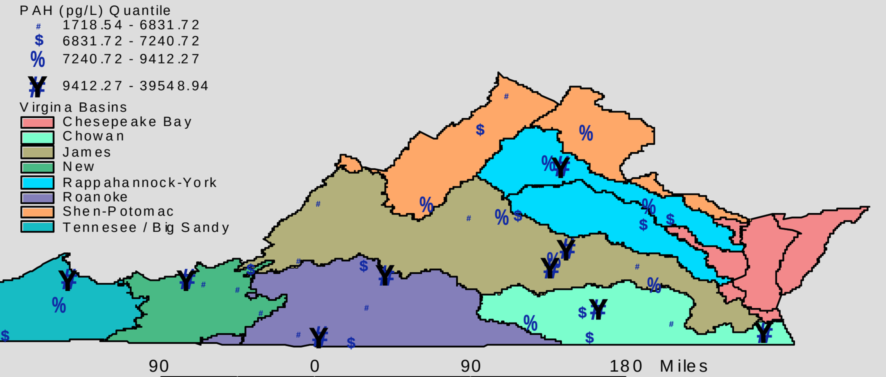


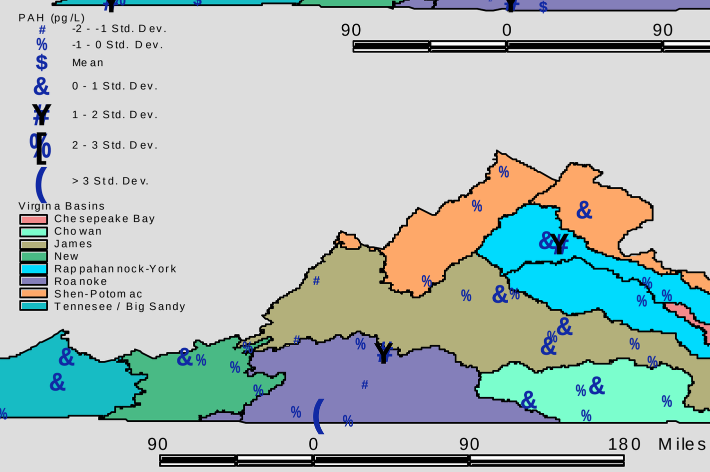


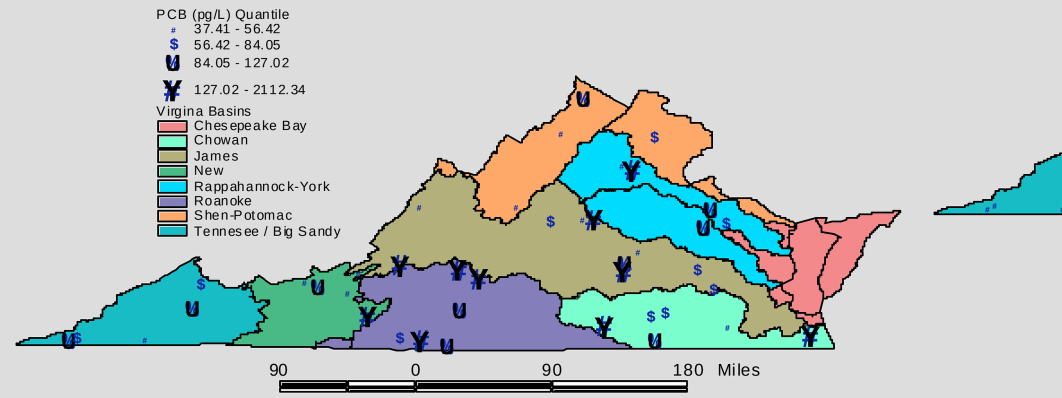
DATA

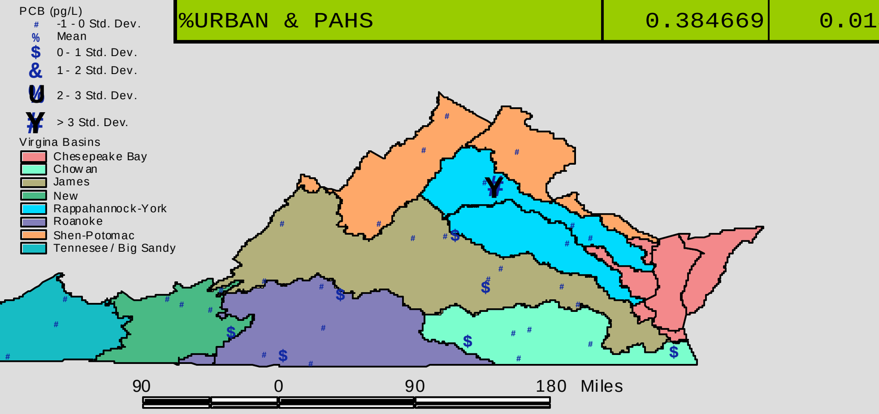
COMPOUNDS WITH WATER QUALITY STANDARDS, pg/L (n=41)	SPMD RESULTS			AQUATIC LIFE				HUMAN HEALTH	
				FRESHWATER		SALTWATER		PUBLIC WATER	ALL OTHER
	MIN	MAX	AVG	ACUTE	CHRONIC	ACUTE	CHRONIC	SUPPLY	SURFACE WATERS
a-Benzenehexachloride	29	122	53					39,000	130,000
Acenaphthene	197	1,402	408					1,200,000,000	2,700,000,000
Anthracene	20	260	62					9,600,000	110,000,000
Benzo[a]anthracene	15	955	87					44,000	490,000
Benzo[a]pyrene	12	218	41					44,000	490,000
Benzo[b]fluoranthene	16	1,654	130					44,000	490,000
Benzo[k]fluoranthene	13	781	73					44,000	490,000
Chlorpyrifos	3	76	17	83,000	41,000	11,000	6		
Chrysene	231	4,227	745					44,000	490,000
Dibenz[a,h]anthracene	16	151	47					44,000	490,000
Dieldrin	7	308	55	240,000	56,000	710,000	1,900	1,400	1,400
Endrin	10	203	26	86,000	36,000	37,000	2,300	760,000	810,000
Fluoranthene	8	15,349	1,049					300,000,000	370,000,000
Fluorene	138	1,369	370					1,300,000,000	14,000,000,000
Heptachlor	0	20	2	520,000	3,800	53,000	3,600	2,100	2,100
Heptachlor Epoxide	14	115	34	520,000	3,800	53,000	3,600	1,000	1,100
Hexachlorobenzene	4	46	17					7,500	7,700
Indeno[1,2,3-c,d]pyrene	13	223	40					44,000	490,000
Lindane	51	177	89	950,000		160,000		190,000	630,000
Methoxychlor	1	329	14		30,000		30,000	100,000,000	
Mirex	0	8	1		0		0		
PCBS	37	2,112	150		14,000		30,000	1,700	1,700
Pentachloroanisole	7	416	110	8,700,000	6,700,000	13,000,000	7,900,000	2,800,000	82,000,000
Pyrene	7	9,853	713					960,000,000	11,000,000,000
CHLORDANE	50	1,388	196	2,400,000	4,300	90,000	4,000	21,000	22,000
DDE	7	166	32					5,900	5,900
DDD	10	270	56					8,300	8,400
DDT	8	189	46	1,100,000	1,000	130,000	1,000	5,900	5,900

NUMBER OF DETECTS ABOVE METHOD DETECTION LIMIT			
Fluoranthene	42	Heptachlor	9
Pentachloroanisole	42	Trans-Permethrin	9
Pyrene	40	d-Benzenehexachloride	8
Trans-Nonachlor	37	Methoxychlor	8
Hexachlorobenzene	33	Oxychlordane	8
Dieldrin	32	Benzo[a]pyrene	7
Perylene	32	Trans-Chlordane	7
cis-Chlordane	30	1,2-dimethylnaphthalene	6
Endosulfan	26	Chrysene	6
2-methylphenanthrene	25	Biphenyl	5
Chlorpyrifos	23	cis-Nonachlor	5
p,p'-DDE	23	Dacthal	5
Endosulfan-II	22	Endosulfan Sulfate	4
o,p'-DDD	22	Indeno[1,2,3-c,d]pyrene	4
p,p'-DDD	22	1-ethylnaphthalene	3
2,3,5-trimethylnaphthalene	20	2-methylnaphthalene	3
Benzo[b]fluoranthene	20	Benzo[g,h,i]perylene	3
Diazinon	20	cis-Permethrin	3
o,p'-DDT	20	Lindane	3
Phenanthrene	20	a-Benzenehexachloride	2
1-methylfluorene	17	PCB, TOTAL	2
Benzo[k]fluoranthene	16	b-Benzenehexachloride	1
Endrin	16	Mirex	1
p,p'-DDT	16	3-methylcholanthrene	0
Benz[a]anthracene	15	4-methylbiphenyl	0
Fluorene	15	9-methylanthracene	0
Anthracene	14	Acenaphthylene	0
1-methylnaphthalene	13	Benzo[b]thiophene	0
Benzo[e]pyrene	13	Dibenz[a,h]anthracene	0
Dibenzothiophene	13	Naphthalene	0
Heptachlor Epoxide	13	o,p'-DDE	0
Trifluralin	13		
3,6-dimethylphenanthrene	12		
Acenaphthene	11		
2-methylfluoranthene	10		
Benzo[b]naphtho[2,1-d]thiophene	10		



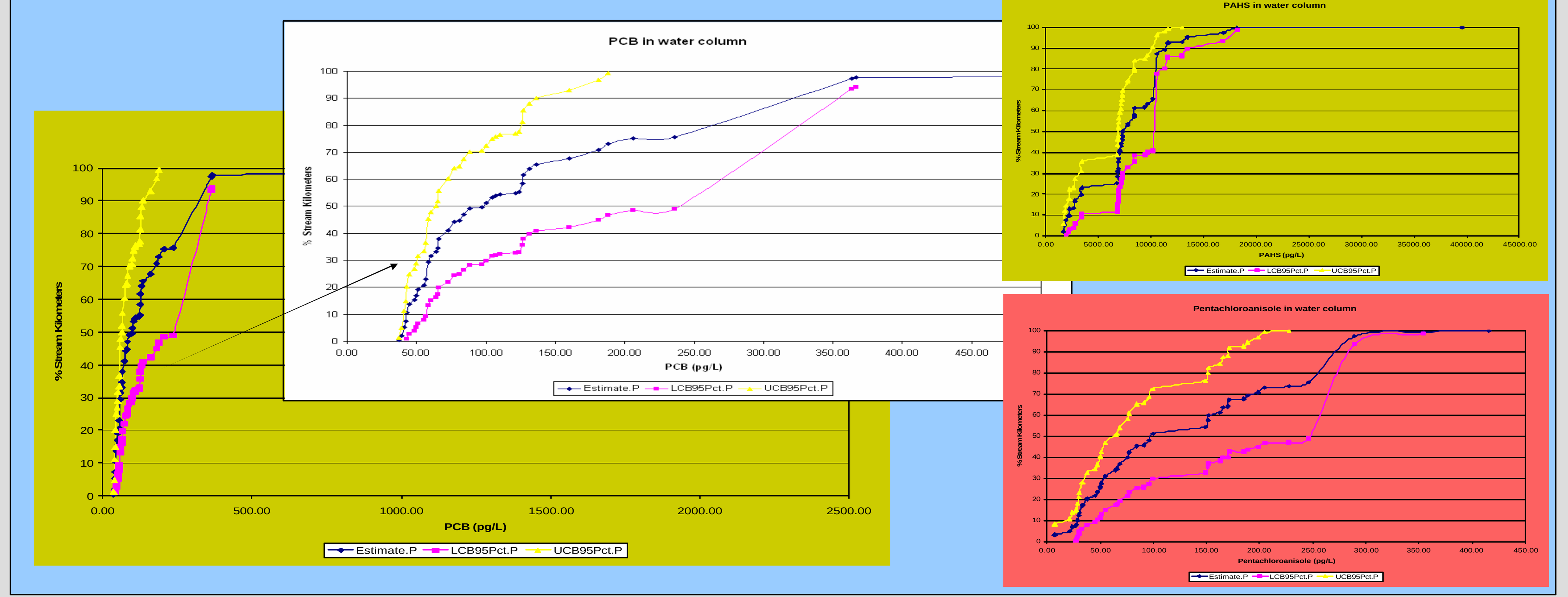






CUMULATIVE DISTRIBUTION FUNCTION

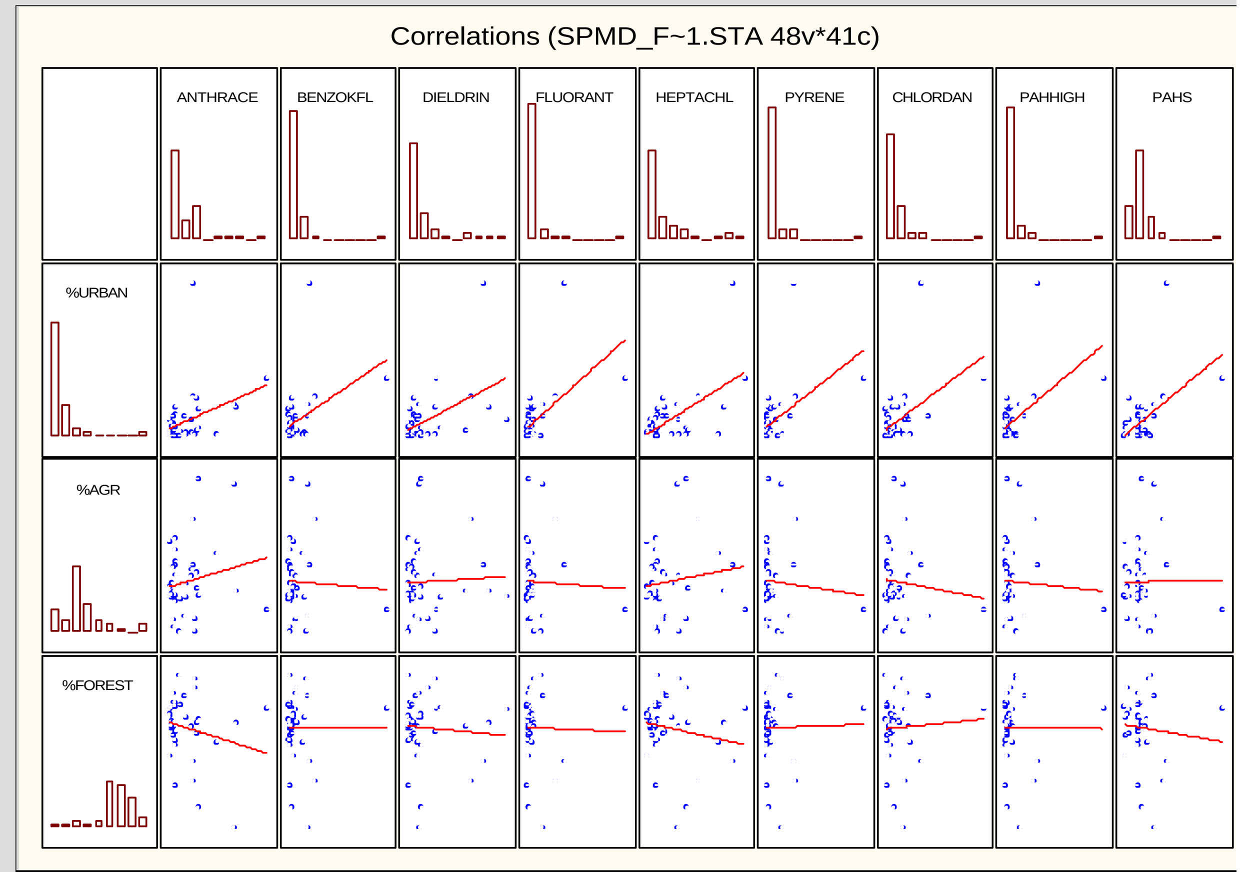
From the generalized random tessellation stratified design, cumulative distribution curves can be used to determine what percent of freshwater streams fall above or below a given concentration.



ANALYSIS

Spearman Rank Correlations		
Parameter	R	p-level
%URBAN & ANTHRACE	0.312034	0.047022
%URBAN & BENZOKFL	0.354806	0.022832
%URBAN & DIELDRIN	0.343902	0.027694
%URBAN & FLUORANT	0.400697	0.009427
%URBAN & HEPTACHL	0.386428	0.012574
%URBAN & PYRENE	0.456272	0.002715
%URBAN & CHLORDAN	0.41899	0.006399
%URBAN & PAHHIGH	0.358014	0.021546
%URBAN & PAHS	0.384669	0.013017

LAND USE CORRELATIONS



SUMMARY

The Water Quality Monitoring, Restoration, and Information Act of Virginia (§ 62.1-44.19:5.) directs the VADEQ to expand geographic and parametric monitoring to include all waters of the state for all compounds which have water quality standards and are of special concern. Given limited financial resources for laboratory analyses, the probabilistic study design meets the objective of expanded geographic coverage. Additionally with the integrative sampling used in this study comparisons to water quality standards were possible because detection limits were sufficient to characterize actual concentrations in the water column.

Residue levels of several chlorinated pesticides (OCP) and polynuclear aromatic hydrocarbon (PAH) in SPMDs were found above the method detection limit at all sites. However, only the concentrations of the OCP pentachloroanisole (PCA) were at or above the method quantitation limit in SPMDs from every site analyzed. Although PCA is classified as an OCP, it is a microbial methylation product of the wood-preservative pentachlorophenol. PCA concentrations detected were well below the water quality standard however it is important to note the widespread occurrence. 80% of the PCP used in the U.S. was for treatment of wood utility poles. In 1987 28 million pounds of PCP were used in the U.S. PCP use was banned in 1987. Because of the large production volumes, the widespread application via utility poles, and the water solubility of PCP it's not surprising to detect widespread PCP contamination in our rivers and streams. A number of the sites had quantifiable levels of some of the other OCPs, which include the chlordanes, the nonachlors, hexachlorobenzene (HCB), dieldrin and endrin. At one site (ID 9-SNK019.59), the concentration of methoxychlor was significantly higher (i.e., eight-fold) than levels found from the next highest site. The highest concentrations of individual PAHs in SPMDs were phenanthrene, fluoranthene and pyrene, which are three of the sixteen PAHs listed by the U.S. Environmental Protection Agency as priority pollutants. This finding is characteristic of the pattern of PAHs emitted from pyrogenic sources. Fluoranthene was present at detectable levels at every site. In several samples, methylated PAHs were also observed, which are characteristic of the pattern of PAHs emitted from petrogenic sources. More than half of the study sites also had detectable levels of at least one of the current-use pesticides. Endosulfans were the most ubiquitous of the current-use pesticides, with detectable levels found at 33 sites. All of the current use pesticides were detected in this study. Every site had one or more detectable concentrations of a current use pesticide.

The study design allowed VADEQ to generate statewide Cumulative Distribution Functions (CDF) curves, which can be used to determine the relationship between concentration and percentage of river miles. Further use of the CDF curves compared the results to our water quality standards. CDF graphs indicate that all hydrophobic organic compounds met state water quality standards except for Polychlorinated Biphenyls (PCB). CDF results estimate that 2% of Virginia streams exceed the state water quality standard of 1700 pg/L for PCB. *It should be noted that nearly 25% of streams are above the 170 pg/L standard recommend by USEPA.*

Further analysis of the probability based data using the Spearman Rank correlation test found that 9 of the 20 parameters with a water quality standard had a moderately significant correlation to increase in watersheds with higher urban components. There was no such trend for agriculture or forest land covers. Intuition from the large volume of data collected by environmental scientists points to urban areas as the greatest source of anthropogenic toxic organics. The importance of this finding is significant because of the statistical power of the sampling design. This study demonstrates that for several key compounds, occurrence and distribution is associated with population density.

Curiosity leads to discovery. Studies sometimes lead to fortunate circumstance where further research is needed. Future sampling at probabilistic sites will examine emerging contaminants.

[1] W.L. Cranor, D.A. Alvarez, S. D. Perkins, G.A. Tegerdine, R.C. Clark, J.N. Huckins, USE OF Semipermeable Membrane Device (Spmd) Technology For A Probabilistic Assessment Of Hydrophobic Organic Contaminants In Selected Reaches Of Virginia Rivers, U.S. Geological Survey, Columbia Environmental Research Center, June 10, 2005.

ACKNOWLEDGEMENTS DEQ: *G.Brown, D.Schmidt, B.Shanabruch, M.Alling, A.Cario, C.Chamberlain, C.Cook, C.French, B.Harrison, G.Holland, L.Seivard, S.Torbeck, D.Smith, M.Shaver, K.Wills, R.Johnson, N.Heagy, E.Cumbow, L.Sparks, A.Silvia, W.Harlan, C.Davey, D.Wolfram, J.Howell, A.Wazlak, W.Van Wart, M.Titman, R.Turner, M.Richardson, R.Anderson, M.Scanlan, A.Barron, D.Lazarus, G.Devlin, D.Miller, G.Anderson, J.Winningham, D.McLeod, T.Liptak, J.Harris, R.Bodkin, T.Frazier, J.Palmore, B.Thomas, A.Grey, S.Cioccia R. Owens.* **USGS:** *Jim Huckins, Dave Alvarez, Randal Clark.,* **EPA:** *Patricia Bradley and Tom Pheiffer for providing the financial support, Tony Olsen - random site selection, weighting, and CDF curve support. Thanks to the generous landowners for allowing DEQ staff access to their property.*