Frequency of Analyte Detections in Environmental Samples

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Introduction

- Environmental measurements
  - ~ wastewaters
  - ~ ground waters
  - ~ surface waters
  - ~ air
  - ~ soil
  - ~ sediment
  - ~ waste materials

- Began in the 1970s and 1980s
  - ~ Clean Water Act, Safe Drinking Water Act, RCRA, Superfund and Clean Air Act.

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- Analytes we measure are based on the requirements established as part of these laws.
  - ~ Priority Pollutant list
  - ~ Appendix 1
  - ~ Appendix 2
  - ~ Appendix 9
  - ~ TCLP toxicity characteristic analytes
- Basically unchanged since their initial publication

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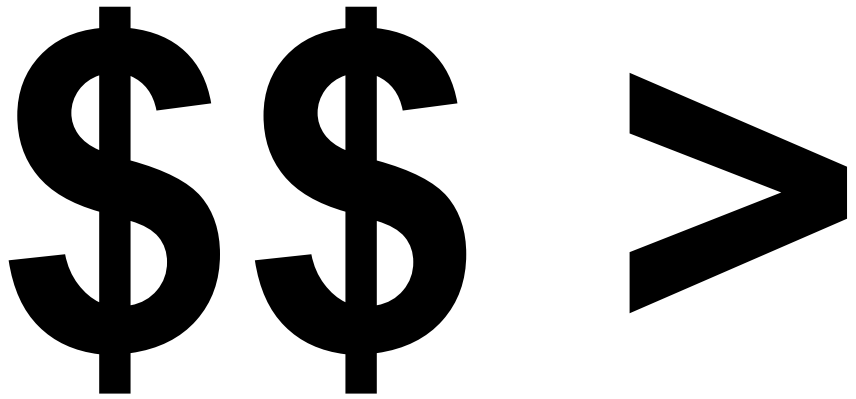
Introduction

- Different
  - ~ Usage of these regulated compounds
  - ~ Environmental releases
  - ~ Environmental persistence of the compounds
- What compounds are routinely found in environmental samples?
- Are there compounds that we invest a lot effort in, but rarely, if ever find?



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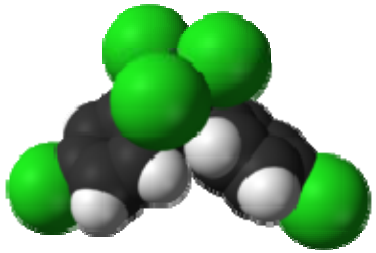
Topics

- The data source and methodology
- Detection frequency by analyte class and by method
  - Pesticides
  - Volatiles
  - Semivolatiles



- A tangent or two
- Quality control requirements for infrequently detected analytes.

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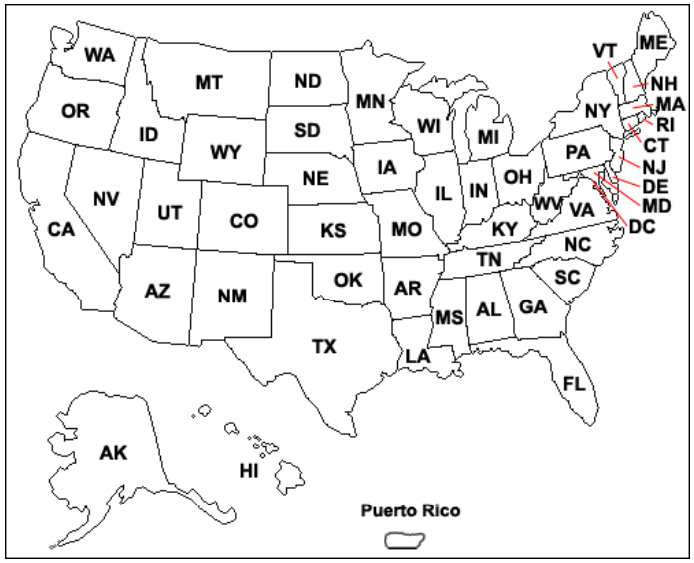
The data source

- All results on client samples for the first 6 months of 2012 in 22 laboratories



Laboratories are in 19 states, but the samples came from all 50 states plus a small amount of overseas samples.

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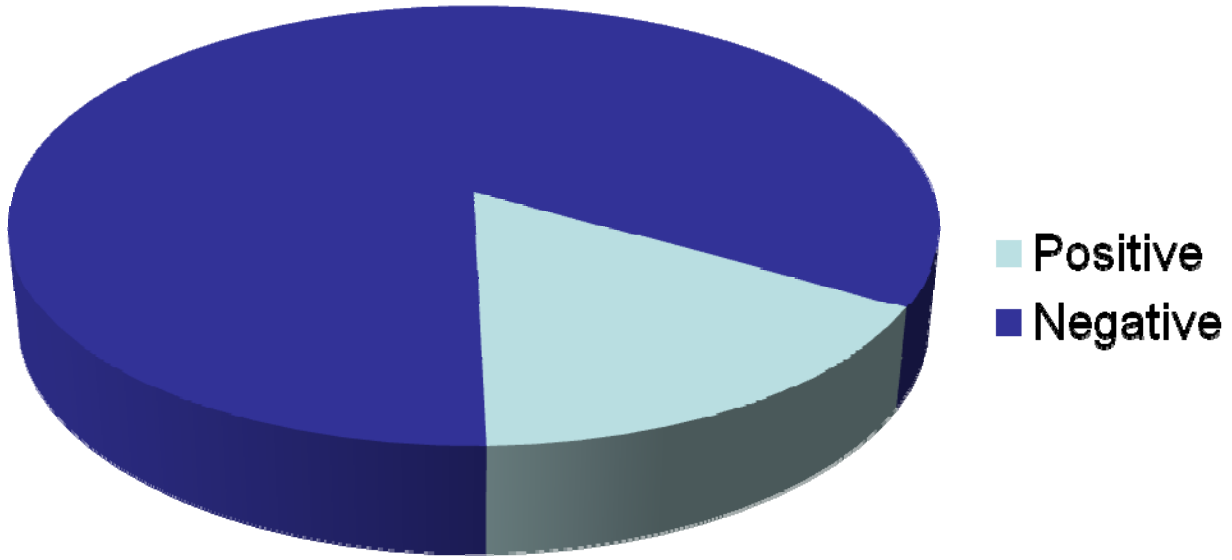
The data source

- 15 M individual measurements
- 2.4 M or 16.3% positive results (above reporting limit)
- Data set - broadly representative
- Excluded internal QC samples and laboratory spiked samples.



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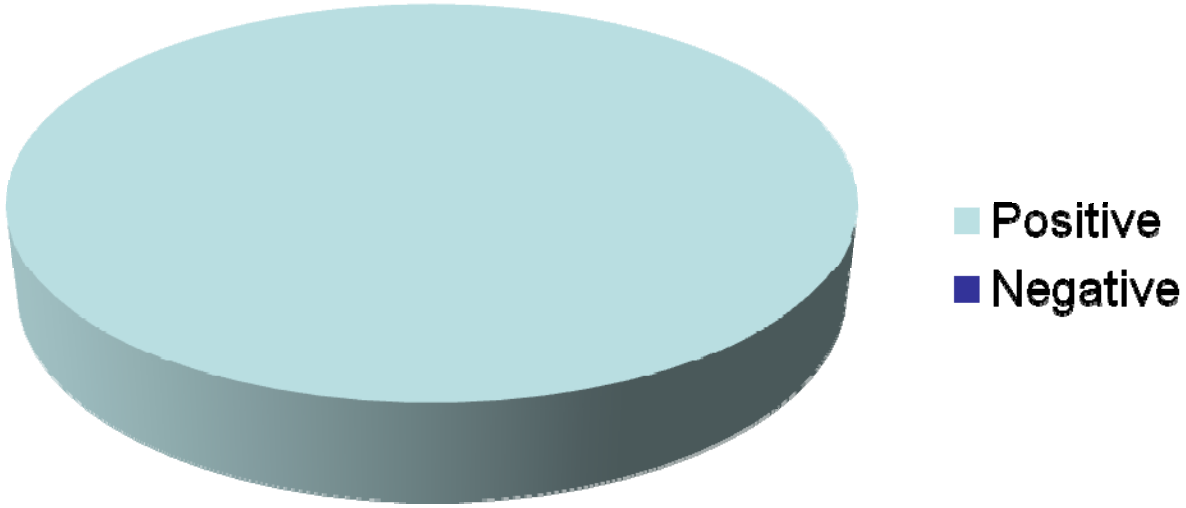
A few examples

- Matrix – Solid
- Requested analysis – Percent solids
- Number of samples – 85,324
- Number of positive results – 85,324 (100%)



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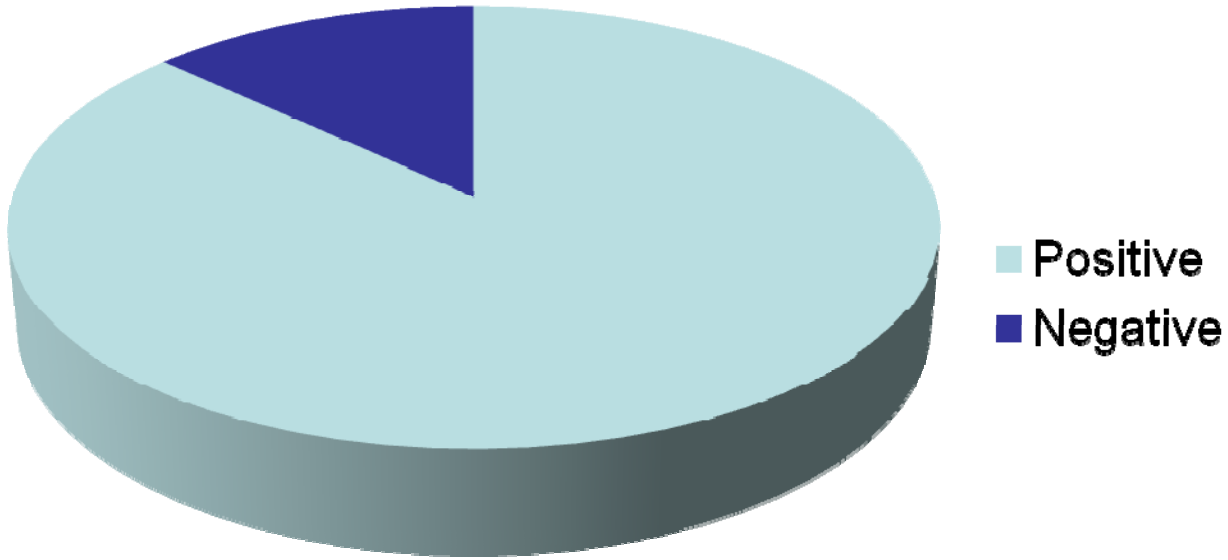
A few examples

- Matrix – Water
- Requested analysis – Sulfate
- Number of samples – 29,269
- Number of positive results – 25,407 (86.8%)



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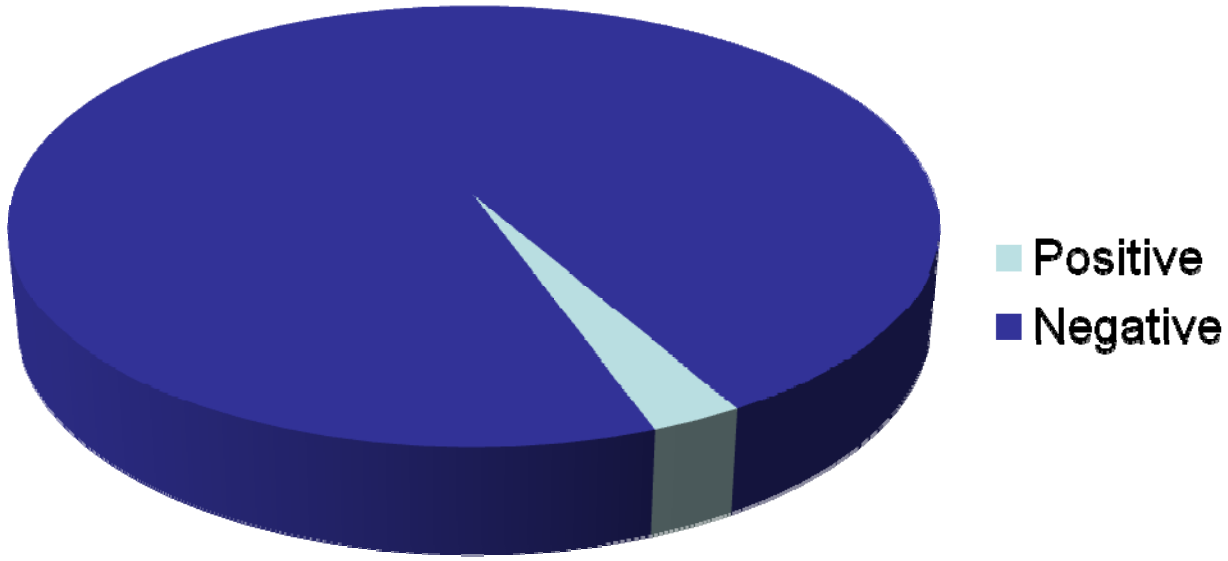
A few examples

- Matrix – Water
- Requested analysis – Silvex
- Number of samples – 3,451
- Number of positive results – 97 (2.8%)



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Pesticides in Sediment

Matrix	Analyte	# samples	# hits	Frequency
Sediment	4,4'-DDE	590	451	76.4%
Sediment	4,4'-DDD	590	443	75.1%
Sediment	4,4'-DDT	590	368	62.4%
Sediment	Endrin	599	325	54.3%
Sediment	2,4'-DDE	414	309	74.6%
Sediment	Methoxychlor	591	291	49.2%
Sediment	Dieldrin	590	274	46.4%
Sediment	Hexachlorobenzene	414	270	65.2%
Sediment	gamma-Chlordane	582	269	46.2%
Sediment	Heptachlor epoxide	599	265	44.2%
Sediment	Endrin ketone	582	247	42.4%
Sediment	trans-Nonachlor	414	235	56.8%
Sediment	alpha-Chlordane	582	234	40.2%
Sediment	Endosulfan II	590	232	39.3%
Sediment	Endosulfan sulfate	590	225	38.1%

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Pesticides in Solids (generally soil)

Matrix	Analyte	# samples	# hits	Frequency
Solid	4,4'-DDT	9796	2012	20.5%
Solid	4,4'-DDE	9772	2010	20.6%
Solid	4,4'-DDD	9772	1085	11.1%
Solid	Dieldrin	11135	1053	9.5%
Solid	gamma-Chlordane	6319	731	11.6%
Solid	alpha-Chlordane	6323	716	11.3%
Solid	Chlordane (technical)	8282	674	8.1%
Solid	Heptachlor epoxide	11215	287	2.6%
Solid	Toxaphene	11248	252	2.2%
Solid	beta-BHC	9317	232	2.5%
Solid	Heptachlor	11192	190	1.7%
Solid	Endrin	11188	155	1.4%
Solid	alpha-BHC	9319	140	1.5%
Solid	gamma-BHC (Lindane)	11235	134	1.2%
Solid	Endrin ketone	8727	129	1.5%
Solid	delta-BHC	9249	127	1.4%
Solid	Aldrin	9431	124	1.3%

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Pesticides in Water

Matrix	Analyte	# samples	# hits	Frequency
Water	beta-BHC	3915	311	7.9%
Water	alpha-BHC	3851	289	7.5%
Water	gamma-BHC (Lindane)	4572	235	5.1%
Water	delta-BHC	3783	222	5.9%
Water	Dieldrin	3928	145	3.7%
Water	4,4'-DDE	3887	102	2.6%
Water	Heptachlor epoxide	4039	99	2.5%
Water	4,4'-DDD	3808	95	2.5%
Water	4,4'-DDT	3939	93	2.4%
Water	gamma-Chlordane	1689	87	5.2%
Water	Endosulfan I	3471	78	2.2%
Water	Heptachlor	4232	76	1.8%
Water	Endrin	4087	75	1.8%
Water	Chlordane (technical)	2622	71	2.7%
Water	4,4-dichlorobenzophenone	75	70	93.3%
Water	Endrin aldehyde	3375	66	2.0%
Water	Endrin ketone	2267	61	2.7%
Water	alpha-Chlordane	1694	59	3.5%
Water	Endosulfan II	3464	52	1.5%
Water	Methoxychlor	4101	49	1.2%

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Pesticide summary

- Found most frequently in sediments
  - ~ Show evidence of environmental conversion
  - ~ Frequently found are highly lipophilic and persistent
- Lower frequency in soils
  - ~ Less evidence of transformation
- Still lower frequency in waters
  - ~ More water soluble pesticides most common
- This all makes sense!

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Volatiles

Matrix	Analyte	# samples	# hits	Frequency
Solid	Ethylbenzene	46969	6075	12.9%
Solid	Xylenes, Total	37436	5612	15.0%
Solid	m-Xylene & p-Xylene	37761	5409	14.3%
Solid	Toluene	47026	5161	11.0%
Solid	o-Xylene	37721	4769	12.6%
Solid	Acetone	27283	4643	17.0%
Solid	Benzene	52539	4073	7.8%
Solid	Trichloroethene	38050	2936	7.7%
Solid	Tetrachloroethene	38151	2803	7.3%
Solid	Methylene Chloride	33416	2543	7.6%
Solid	1,2,4-Trimethylbenzene	18406	2412	13.1%
Solid	Naphthalene	18047	2176	12.1%
Solid	cis-1,2-Dichloroethene	32191	2164	6.7%
Solid	Isopropylbenzene	24877	1934	7.8%
Solid	1,3,5-Trimethylbenzene	17678	1859	10.5%
Solid	N-Propylbenzene	14420	1319	9.1%
Solid	2-Butanone (MEK)	32419	1210	3.7%
Solid	n-Butylbenzene	14652	1001	6.8%
Solid	4-Isopropyltoluene	14054	908	6.5%
Solid	Methyl tert-butyl ether	34873	844	2.4%

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Infrequently Detected Volatiles

Matrix	Analyte	# samples	# hits	Frequency
Solid	Bromomethane	31946	105	0.3%
Solid	Dichlorodifluoromethane	23928	80	0.3%
Solid	Tert-amyl methyl ether	4734	8	0.2%
Solid	Tert-butyl ethyl ether	4731	6	0.1%
Solid	1,3-Dichloropropene, Total	3013	1	0.0%
Water	Dibromomethane	44159	120	0.3%
Water	Chlorobromomethane	45814	118	0.3%
Water	1,1-Dichloropropene	33307	114	0.3%
Water	cis-1,3-Dichloropropene	74957	109	0.1%
Water	1,2-Dibromo-3-Chloropropane	52636	92	0.2%
Water	2,2-Dichloropropane	33162	89	0.3%
Water	Methyl acetate	14591	39	0.3%
Water	Iodomethane	16034	35	0.2%
Water	Vinyl acetate	25619	30	0.1%
Water	Ethyl methacrylate	6110	14	0.2%
Water	3-Chloro-1-propene	5322	10	0.2%
Water	2-Chloro-1,3-butadiene	4247	2	0.0%
Water	trans-1,4-Dichloro-2-butene	14571	1	0.0%
Water	1,3-Dichloropropene, Total	3385	0	0.0%

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Semivolatiles

Matrix	Analyte	# samples	# hits	Frequency
Sediment	Benzo[b]fluoranthene	1041	824	79.2%
Sediment	Pyrene	1041	799	76.8%
Sediment	Fluoranthene	1041	792	76.1%
Sediment	Chrysene	1041	783	75.2%
Sediment	Phenanthrene	1041	770	74.0%
Sediment	Benzo[a]anthracene	1041	765	73.5%
Sediment	Benzo[a]pyrene	1041	765	73.5%
Sediment	Indeno[1,2,3-cd]pyrene	1041	750	72.0%
Sediment	Benzo[g,h,i]perylene	1041	737	70.8%
Sediment	Anthracene	1041	676	64.9%
Sediment	Dibenz(a,h)anthracene	1041	610	58.6%
Sediment	Naphthalene	1041	602	57.8%
Sediment	Acenaphthene	1032	555	53.8%
Sediment	Benzo[k]fluoranthene	1041	552	53.0%
Sediment	Acenaphthylene	1041	546	52.4%
Sediment	Fluorene	1041	531	51.0%
Sediment	2-Methylnaphthalene	799	469	58.7%
Sediment	Bis(2-ethylhexyl) phthalate	659	379	57.5%
Sediment	Carbazole	652	206	31.6%
Sediment	Dibenzofuran	652	117	17.9%

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Solids

Matrix	Analyte	# samples	# hits	Frequency
Solid	Benzo[b]fluoranthene	30404	8992	29.6%
Solid	Benzo[a]pyrene	30877	8393	27.2%
Solid	Benzo[a]anthracene	30632	8357	27.3%
Solid	Pyrene	30297	8234	27.2%
Solid	Fluoranthene	29865	7942	26.6%
Solid	Phenanthrene	29914	7461	24.9%
Solid	Chrysene	30504	7149	23.4%
Solid	Indeno[1,2,3-cd]pyrene	30131	6895	22.9%
Solid	Benzo[k]fluoranthene	29682	6603	22.2%
Solid	Benzo[g,h,i]perylene	29628	5642	19.0%
Solid	Anthracene	30294	3889	12.8%
Solid	Dibenz(a,h)anthracene	29881	3765	12.6%
Solid	Naphthalene	31140	3702	11.9%
Solid	Fluorene	30107	2855	9.5%
Solid	2-Methylnaphthalene	26225	2777	10.6%
Solid	Acenaphthene	29931	2273	7.6%
Solid	Acenaphthylene	29339	1799	6.1%
Solid	Bis(2-ethylhexyl) phthalate	20112	1746	8.7%

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Waters

Matrix	Analyte	# samples	# hits	Frequency
Water	Naphthalene	19448	3604	18.5%
Water	2-Methylnaphthalene	16685	2412	14.5%
Water	1-Methylnaphthalene	5716	1533	26.8%
Water	Acenaphthene	18221	1460	8.0%
Water	Fluorene	17929	1267	7.1%
Water	Phenanthrene	18194	1243	6.8%
Water	1,4-Dioxane	3094	937	30.3%
Water	Phenol	12349	932	7.5%
Water	Pyrene	18250	730	4.0%
Water	Fluoranthene	17914	717	4.0%
Water	Benzo[a]anthracene	18288	605	3.3%
Water	Naphthalene	2132	593	27.8%
Water	Bis(2-ethylhexyl) phthalate	12143	570	4.7%
Water	3 & 4 Methylphenol	7146	540	7.6%
Water	Anthracene	18037	537	3.0%
Water	Benzo[b]fluoranthene	18075	533	2.9%
Water	2-Methylphenol	11542	505	4.4%
Water	Phenanthrene	2046	484	23.7%
Water	Acenaphthylene	17373	478	2.8%
Water	2,4-Dimethylphenol	11386	443	3.9%
Water	Benzo[a]pyrene	18347	423	2.3%
Water	Benzo[a]anthracene	4256	408	9.6%

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An oddity

Matrix	Analyte	# samples	# hits	Frequency
Solid	4-Chlorophenyl phenyl ether	18373	37	0.2%
Solid	4-Bromophenyl phenyl ether	18609	33	0.2%

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Flame retardants

- Generally one hit for each in each laboratory
- One lab with about a dozen hits
- Hits appear to be in the same sample
- Possible explanations
  - ~ Lightning struck the same place 33 times
  - ~ Solid material that contains both flame retardants that is widely distributed so it occasionally shows up in environmental samples
  - ~ These are PE samples

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Tangent #1 – how not to make "blind" PE samples

- Use a fictitious company name – the PM will know within minutes
- Add a collection of compounds all within a reasonable and typical calibration range
- Spike with analytes that are rarely found
- Spike one of the 5 ring PAHs and leave all the others out
- Spike one of the brominated trihalomethanes without the others
- Put bromoform in a solid sample
- Any illogical collection of analytes

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Back to the topic at hand

- Some analytes are detected frequently,
- Distribution between solids and waters is consistent with our understanding of their distribution and their environmental fate chemistry.
- Many analytes are rarely if ever found

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Will we ever detect any of these?

Matrix	Analyte	# samples	# hits	Frequency
Water	1,2,4,5-Tetrachlorobenzene	3476	0	0.0%
Water	p-Dimethylamino azobenzene	1756	0	0.0%
Water	1,3,5-Trinitrobenzene	1589	0	0.0%
Water	1,4-Naphthoquinone	1529	0	0.0%
Water	3,3'-Dimethylbenzidine	1532	0	0.0%
Water	3-Methylcholanthrene	1675	0	0.0%
Water	4-Aminobiphenyl	1560	0	0.0%
Water	4-Nitroquinoline-1-oxide	852	0	0.0%
Water	7,12-Dimethylbenz(a)anthracene	1796	0	0.0%
Water	Chlorobenzilate	1277	0	0.0%
Water	Ethyl methanesulfonate	1670	0	0.0%
Water	Hexachlorophene	526	0	0.0%
Water	Hexachloropropene	1589	0	0.0%
Water	Methapyrilene	1556	0	0.0%
Water	Methyl methanesulfonate	1582	0	0.0%
Water	N-Nitrosodiethylamine	1635	0	0.0%
Water	N-Nitrosomethylethylamine	1542	0	0.0%
Water	N-Nitrosopiperidine	1661	0	0.0%
Water	Pentachloroethane	727	0	0.0%
Water	p-Phenylene diamine	1482	0	0.0%
Water	Safrole, Total	1536	0	0.0%

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What method performance do we need for these?

Matrix	Analyte	# samples	# hits	Frequency
Solid	Hexachlorocyclopentadiene	18383	1	0.0%
Solid	Ethyl methanesulfonate	967	1	0.1%
Solid	N-Nitrosodiethylamine	945	1	0.1%
Solid	Pentachlorobenzene	1316	1	0.1%
Water	1,3-Dinitrobenzene	1625	2	0.1%
Water	N-Nitrosodi-n-butylamine	1814	2	0.1%
Water	Pronamide	1743	2	0.1%
Water	Pentachlorobenzene	1913	1	0.1%
Water	Pentachloronitrobenzene	1951	1	0.1%
Water	1-Naphthylamine	1656	1	0.1%
Water	2-Acetylaminofluorene	1544	1	0.1%
Water	Dimethoate	1261	1	0.1%
Water	Disulfoton	1108	1	0.1%
Water	Ethyl Parathion	1053	1	0.1%
Water	Famphur	1207	1	0.1%
Water	Isodrin	917	1	0.1%
Water	Isosafrole	1537	1	0.1%
Water	N-Nitrosomorpholine	850	1	0.1%
Water	Phenacetin	1658	1	0.1%
Water	Phorate	1099	1	0.1%
Water	Sulfotepp	725	1	0.1%
Water	Thionazin	1103	1	0.1%

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Should this influence our analytical approach?

- Florida direct contact residential risk based limits

Analyte	Risk Based Limit (mg/Kg)	Typical RL (mg/Kg)	Detection Frequency
hexachlorocyclopentadiene	9.5	0.3	0.0%
2 nitroaniline	24	0.3	0.1%
3-nitroaniline	21	0.3	0.0%
2,4-dinitrophenol	110	0.3	0.0%
bis(2-chloroisopropyl)ether	6	0.3	0.1%
4,6-Dinitro-2-methylphenol	8.4	0.3	0.0%
Hexachlorobutadiene	6.4	0.3	0.2%

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Questions

- For analytes that are rarely if ever detected…
  - ~ Do we need a five point curve?
  - ~ Do we need a spike in the mid range of the calibration?
  - ~ Do we need to detect the analyte at the maximum sensitivity of the instrument or should we target some fraction of the risk based concentration limit?

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Presence or Absence Analysis

- Verify adequate recovery at 10% or less of the risk based limit for each infrequently detected analyte
- Do a single point calibration at this level or lower when that analyte is requested
- If the analyte is detected at a concentration (based on the single point calibration) that is greater than 20% of the regulatory limit, do a full five point curve and reanalyze.
- Better data at the concentration range of interest

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An example

- Infrequently detected analyte
- Quadratic calibration – all calibration and batch quality control perfect
- C = -5X2 + 8.42X -4.83
- Client submitted PE sample 3X the top of the calibration range but below the regulatory limit
- Equation gives a negative number, instrument software give “ND”.
- Serious risk of false negative in this case.
- Minimal risk of false negative with “presence or absence” analysis.

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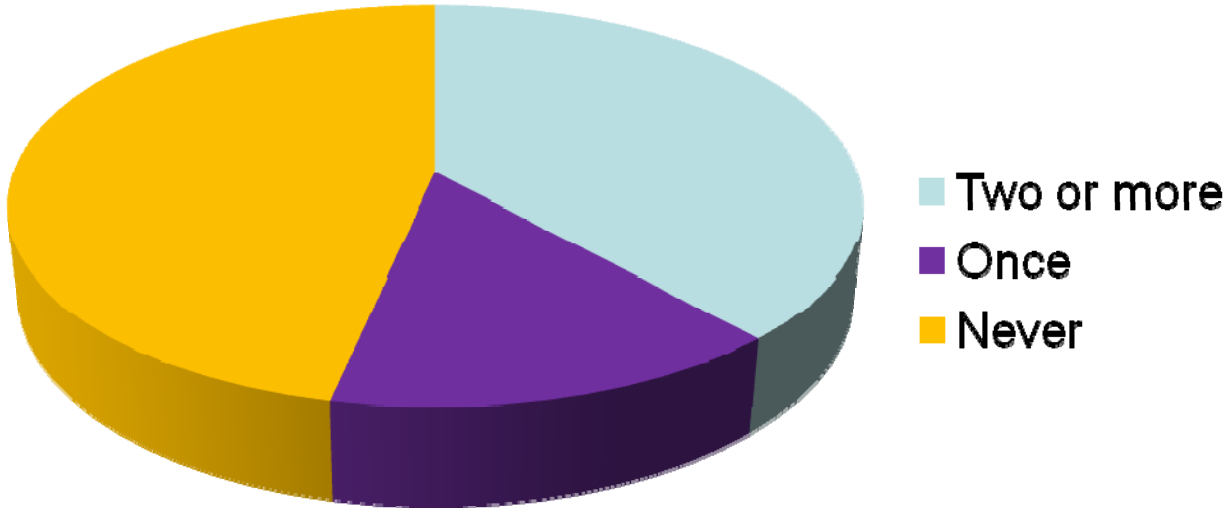
Less Expensive

- Laboratories in this data set
  - ~ 420 analytes in water samples using method 8270.
  - ~ 196 have never been detected
  - ~ 63 have only been detected once.
- All of them have 5 point curves, MDL studies, and initial demonstrations of capability.



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Summary and Conclusions

- Most organic analytes almost never found
- Maintaining full quantitative capabilities has no benefit for these analytes
- Presence / Absence test for < 10% of risk based level
  - Less risk of false negative
  - More cost effective