Measuring Polychlorinated Biphenyls (PCB) in Soils and Solvent Extracts Using Field Analytical Techniques

Presented by

U.S. Environmental Protection Agency's (EPA)
Technology Innovation Office (TIO) and
Office of Research and Development (ORD) and the
Department of Energy's (DOE)
Oak Ridge National Laboratory (ORNL)

EPA

Environmental Technology Verification (ETV) Program

- Established by EPA to verify environmental technologies
- Goal = to advance environmental protection by accelerating the acceptance and use of improved and more cost-effective technologies
- ETV pilot programs involve partners from both the public and private sector to test new technologies under EPA oversight
- Currently there are 12 pilot programs including the Site Characterization and Monitoring Technologies pilot program
- For the Site Characterization and Monitoring Technologies pilot program, EPA actively partners with DOE's ORNL and Sandia National Laboratory (SNL)

Site Characterization and Monitoring Technology Pilot Program

- ORD's NERL manages implementation of the program with support from TIO
- Goal = to increase the application of innovative site characterization technologies
- Pilot objectives:
  - Define a process for verifying technology performance
  - Information transfer
- Administered by the National Exposure Research Laboratory (NERL) Environmental Sciences Division (ESD) in Las Vegas, Nevada and managed by EPA's ORD

Verification of PCB Field Analytical Techniques

- Purpose = to verify field analytical techniques capable of detecting and quantifying PCBs in soils and solvent extracts which mimic surface wipe samples
- Demonstration objectives:
  - Obtain performance information using environmental and quality control (QC) samples
  - Compare field results with conventional laboratory results
  - Report on logistical operation of the technology
- The demonstration evaluated performance under two distinct site conditions, using a special controlled environmental chamber available at ORNL
- Data used in this session excerpted from ETV reports

Demonstration Study Plan

- Two sets of environmental conditions
  - Outdoors, naturally variable temperature and relative humidity
  - Controlled environmental chamber, constant temperature and relative humidity
- Samples
  - Performance evaluation (PE) soil (n=72)
  - Environmental soil (n=136)
  - Simulated extract (n=24)
- Concentration range
  - PE Soil: 0 to 50 parts per million (ppm)
  - Environmental Soil: 0.1 to 700 ppm
  - Simulated extract: 0 to 100 µg/mL (simulated wipe concentration: µg/100cm^2)

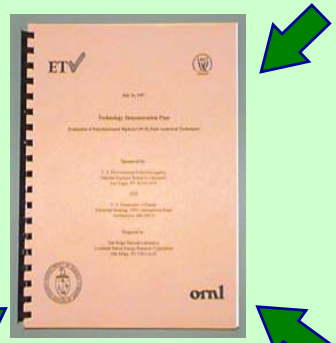
Seven Technologies Evaluated

- Immunoassay test kits
  - RaPID Assay (Strategic Diagnostics Inc. (SDI))
  - D TECH (SDI)
  - Envirogard (SDI)
  - PCB Immunoassay Kit (Hach Company)
  - PCB in Soil Tube Assay (EnviroLogix Inc.)
- Gas chromatography/surface acoustic wave (GC/SAW) detector
  - 4100 Vapor Detector (Electronic Sensor Technology)
- Ion-specific electrode-based chemical test kit
  - L2000 PCB/Chloride Analyzer (Dexsil Corporation)

Overview of Environmental Technology Verification Process

Statisticians

Project Officers



Chemists

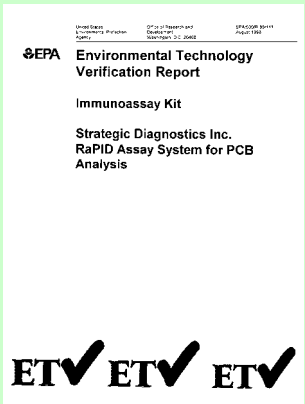
Stakeholders

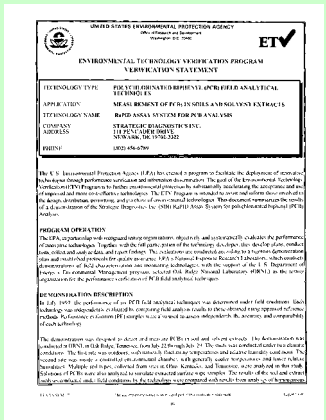
Experimental Plan

Samples are collected, homogenized, labeled, and assembled for distribution.

ETV

Technology developers analyze randomized samples under field conditions.





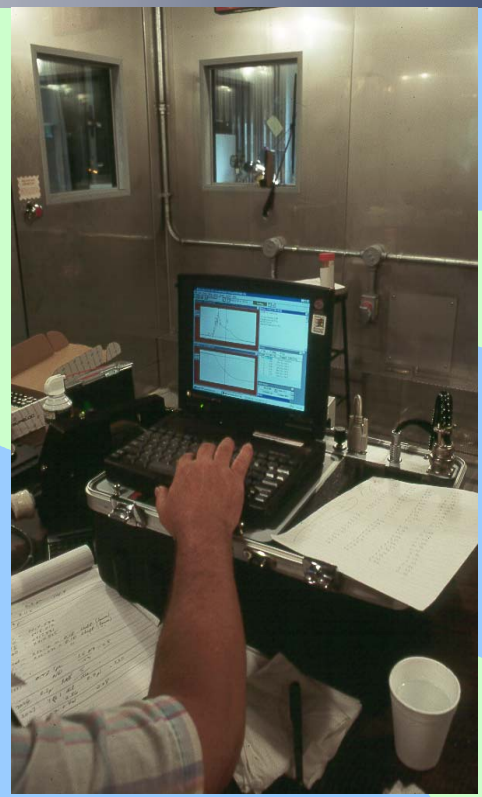
Product is report and verification statement.

Each Developer Analyzed 232 samples During the Demonstration

- ✓ 112 real environmental soil samples
- ✓ 24 spiked environmental soil samples
- ✓ 16 commercially-prepared performance evaluation (PE) soil samples
- ✓ 48 EPA-prepared PE soil samples
- ✓ 24 ORNL-prepared PCB extracts
- ✓ 8 uncontaminated samples

Developers Analyzed 116 Samples for Each Technology at Each of Two "Sites"

Environmental Chamber and Separate Sample Suite Simulated Second Site with Huge Cost/Time Savings



Terms Explained

Detection Limits	Method Detection Limit (MDL) or lowest reporting interval
Sample throughput rate	Samples/hour/number of analysts.
False positive results	Frequency with which the test system reports as a detect for samples which are confirmed to have no target analyte present.
False negative results	Number of non-detects by the test systems when PCBs were detected by the reference laboratory method.

Terms Explained

Precision	Average relative standard deviation on replicate samples or the fraction of sample sets where number of replicates reported within the same interval.
Accuracy	Average percent recovery or fraction in agreement with a "known" test sample
Comparability	Results relative to reference laboratory results

Immunoassay—Theory of Operation

- Antibody-target analyte interaction
- Fits “lock and key” model
- Quantitation performed by monitoring color change

Immunoassay — Method Description

- Antibody coating
- Sample and enzyme conjugate addition
- Competitive binding reaction
- Color formation
- Measurement of color

Immunoassay — Advantages

- Field portable
- Requires little training time
- Relatively high sample throughput
- Inexpensive
- Can be used for a wide range of analytes

Immunoassay — Limitations

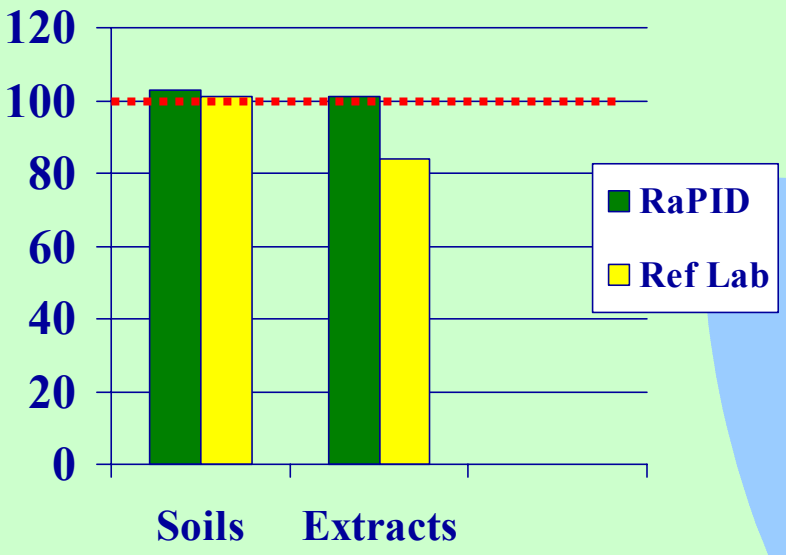
- Prior knowledge of analytes present at a site is helpful
- Reagents may require refrigeration
- Possible cross reactivity to similar compounds (false positives)
- Semiquantitative analysis in some cases
- Long development time for new antibodies and methods

Five Immunoassay Test Kits Evaluated

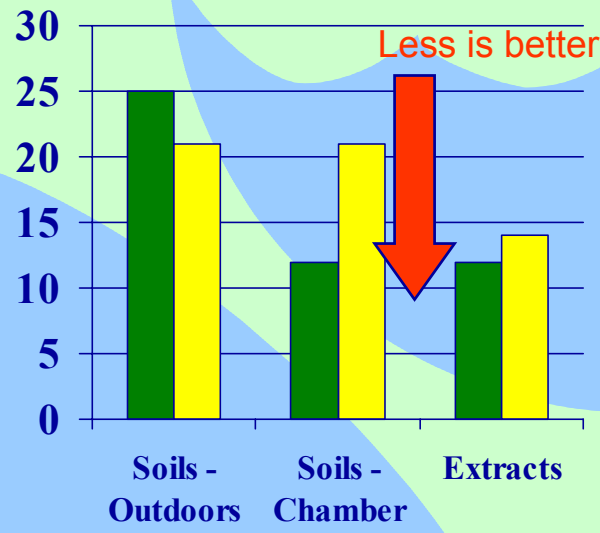
- RaPID
- D TECH
- Envirogard
- PCB Immunoassay Kit
- PCB in Soil Tube Assay

SDI
RaPID Assay System

Accuracy, %

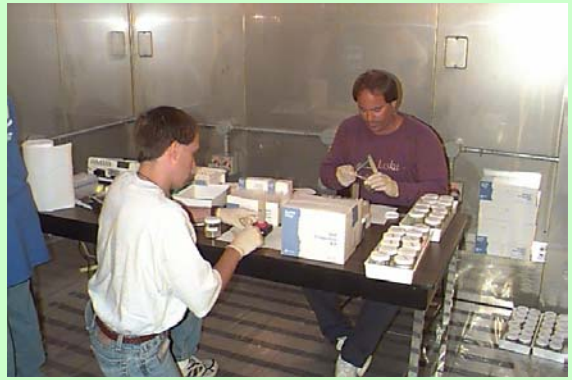


Precision, RSD,%



EPA

SDI
RaPID Assay System



Comparability: $R^2 = 0.754$ (soils); $R^2 = 0.977$ (extracts)

False positive results: 0% (0 of 8 soils); 0% (0 of 8 extracts)

False negative results: 1% (2 of 192 soils); 0% (0 of 16 extracts)

Detection limits: 1.5 ppm

Throughput (3 analysts): 10 - 11 samples/h

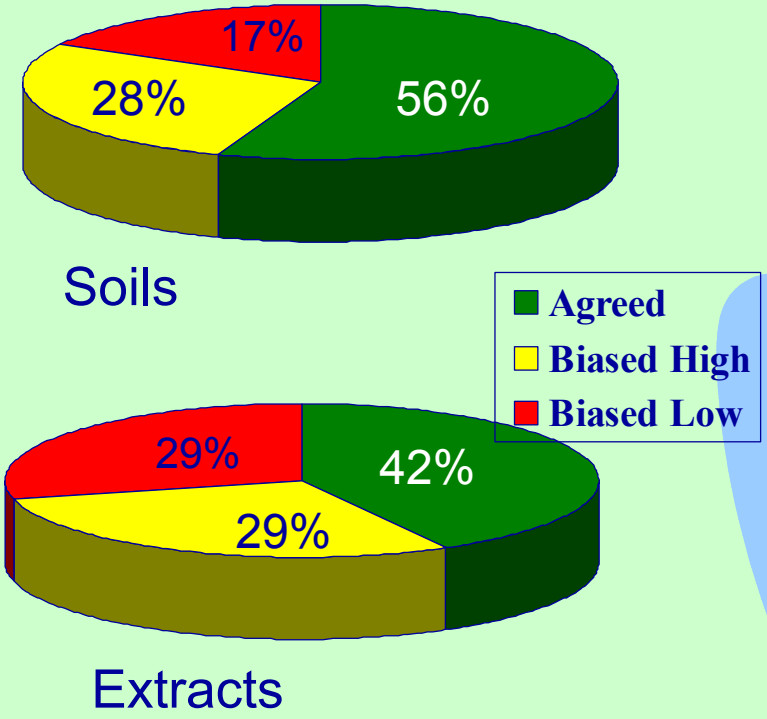
RaPID Assay System for PCB Analysis — SDI

		50 ppm (soils)	100 µg/100cm^2 (extract)
Regulatory levels			
	RSD (precision):	21%	12%
	Percent recovery (accuracy):	126%	101%
Data quality	Precise and slightly biased		

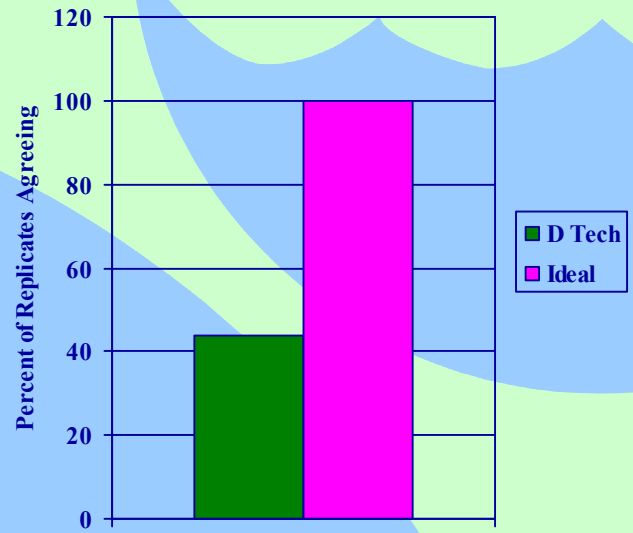
SDI
D TECH PCB Test Kit

Interval Data

Accuracy, %



Precision of Replicates



EPA

SDI
D TECH PCB Test Kit

Comparability: 53% agreed; 28% biased high; 20% biased low (soils)
42% agreed; 29% biased high; 29% biased low (extracts)

False positive results: 62% (5 of 8 soils); 25% (2 of 8 extracts)

False negative results: 0.5% (1 of 192 soils); 0% (0 of 16 extracts)

Detection limits: lowest reporting interval (0 to 0.5 ppm)

Throughput (3 analysts): 11 samples/h (chamber)
15 samples/h (outdoor)

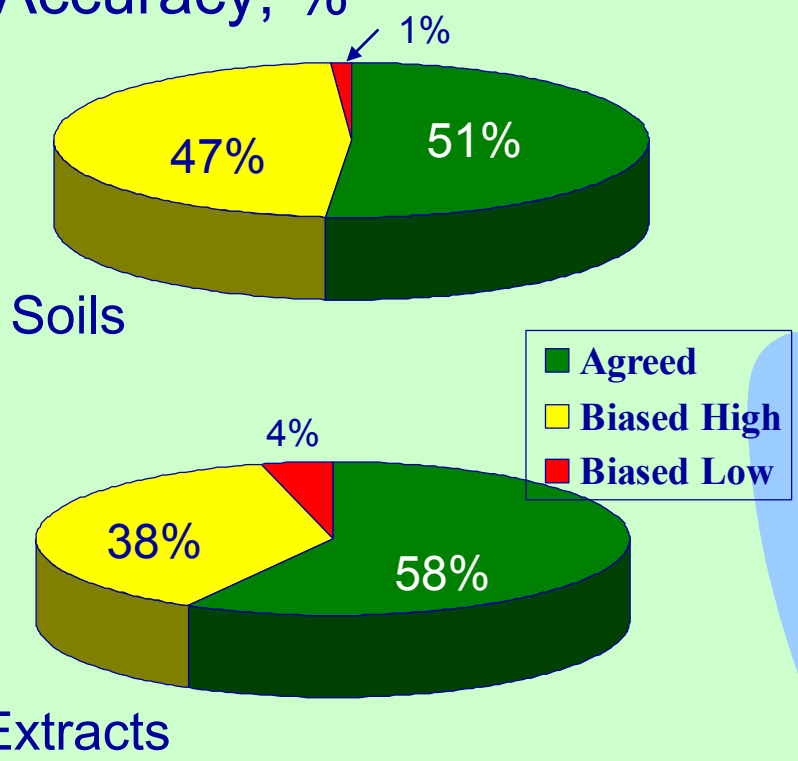
D TECH PCB Test Kit — SDI

Regulatory levels		50 ppm (soil)	100 µg/100 cm^2 (extract)
	Agreed:	61%	42%
	Biased high:	7%	29%
	Biased low:	32%	29%
Data quality	Imprecise and biased high and low		

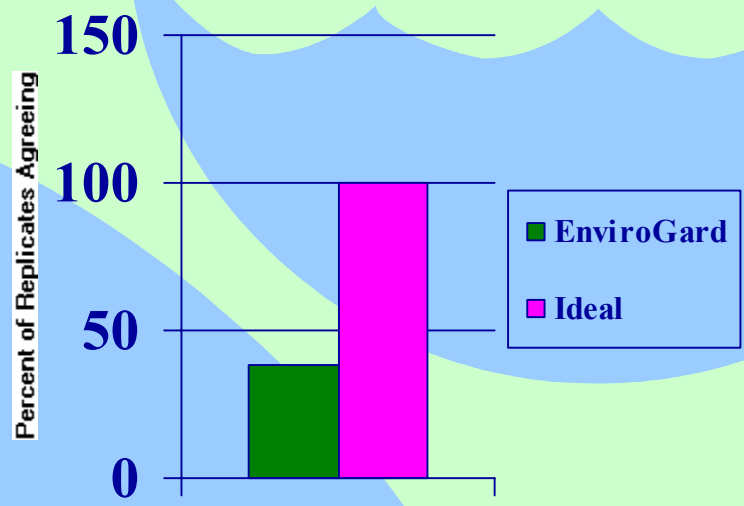
SDI
EnviroGard PCB Test Kit

Interval Data

Accuracy, %



Precision of Replicates



EPA

SDI
EnviroGard PCB Test Kit

Comparability: 53% agreed; 45% biased high; 2% biased low (soils)
63% agreed; 38% biased high; 0% biased low (extr)

False positive results: 0% (0 of 8 soils); 13% (1 of 8 extracts)

False negative results: 0% (0 of 192 soils); 0% (0 of 16 extracts)

Detection limits: lowest reporting interval (0 to 1 ppm)

Throughput (3 analysts) : 9-10 samples/h (chamber)
18 samples/h (outdoor)

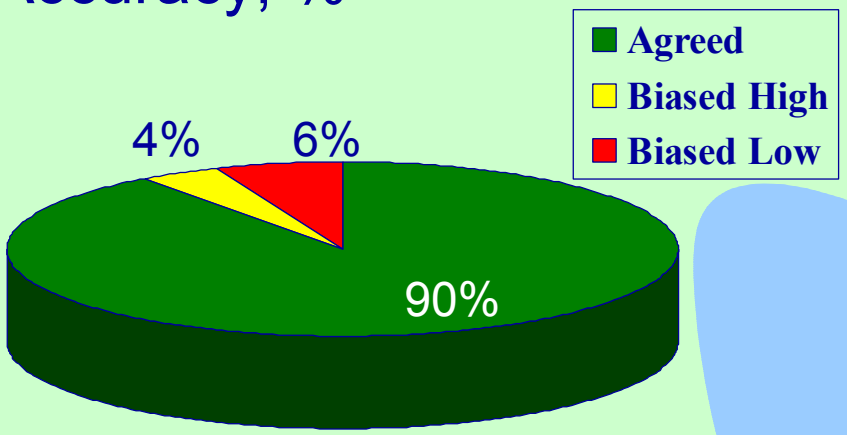
EnviroGard PCB Test Kit — SDI

		50 ppm (soil)	100 µg/cm^2 (extract)
Regulatory levels	Agreed:	39%	63%
	Biased high:	59%	38%
	Biased low:	2%	4%
Data quality	Imprecise and biased high		

Hach
PCB Immunoassay Kit

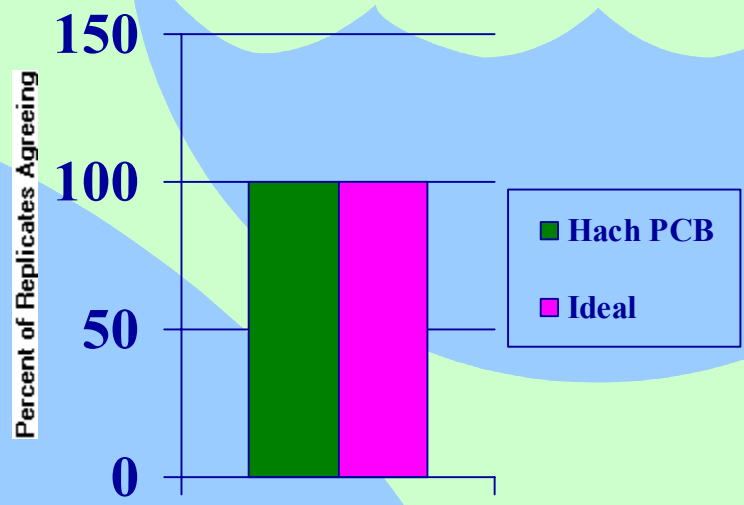
Interval Data

Accuracy, %



Soils

Precision of Replicates



EPA

Hach
PCB Immunoassay Kit

Comparability: 85% agreed; 7% biased high; 9% biased low (soils)

False positive results: 38% (3 of 8 soils)

False negative results: 2% (4 of 192 soils)

Detection limits: lowest reporting interval (0 to 1 ppm)

Throughput (2 analysts): 7-10 samples/h (chamber)
10-13 samples/h (outdoor)

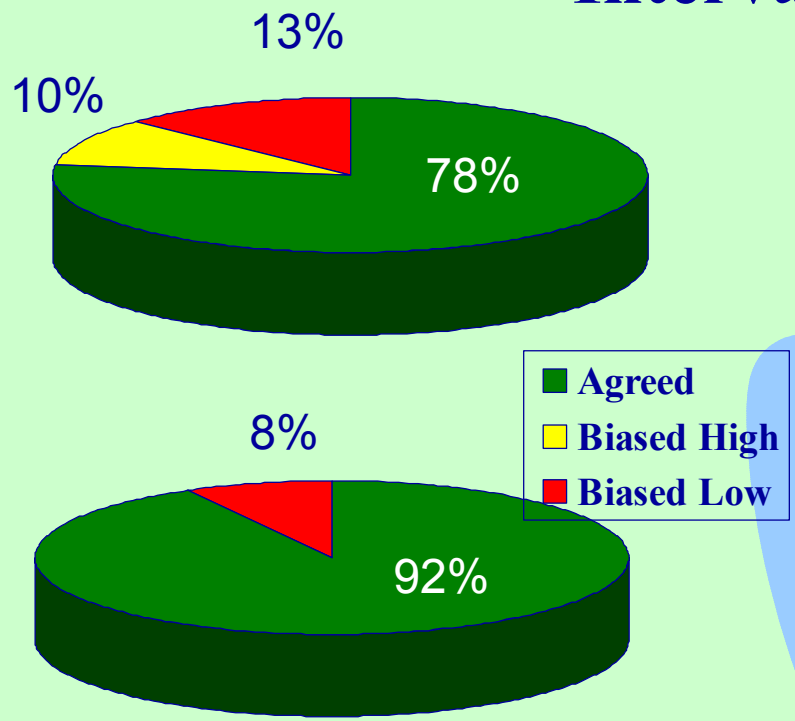
PCB Immunoassay Kit — Hach Company

Regulatory levels	Agreed:	98%
	Biased high:	0%
	Biased low:	2%
Data quality	Precise and unbiased	

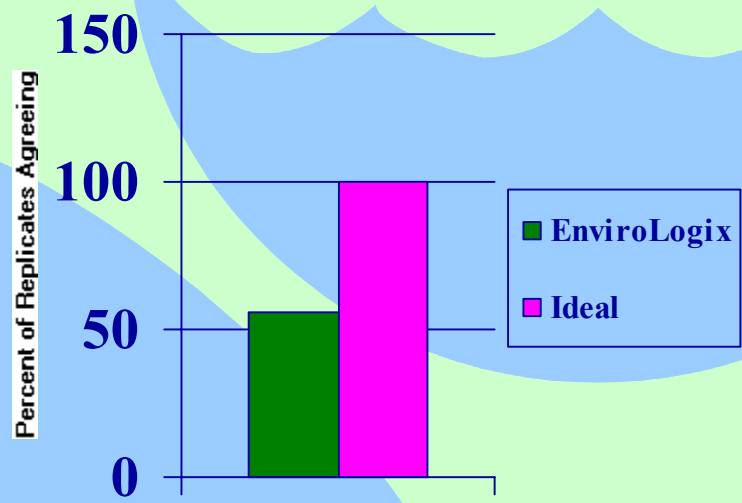
EnviroLogix
PCB in Soil Tube Assay

Interval Data

Accuracy, %



Precision of Replicates



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EnviroLogix
PCB in Soil Tube Assay

Comparability: 82% agreed; 12% biased high; 7% biased low (soils)

False positive results: 0% (0 of 8 soils); 0% (0 of 8 extracts)

False negative results: 4% (7 of 192 soils); 0% (0 of 16 extracts)

Detection limits: lowest reporting interval (0 to 1 ppm)

Throughput (1 analyst): 7 samples/h (chamber)
8 samples/h (outdoor)

PCB in Soil Tube Assay — EnviroLogix Inc.

Regulatory levels	Agreed:	66%
	Biased high:	32%
	Biased low:	2%
Data quality	Imprecise and unbiased	

Gas Chromatograhy/Surface Acoustic Wave (SAW) Detector

- One instrument evaluated—4100 Vapor Detector by Electronic Sensor Technology
- General theory of operation presented for GC
- More detailed information presented for SAW detectors

Gas Chromatography (GC)

- Designed to “resolve” or separate a mixture of compounds (usually organic)
- Relies on the solubility of the analyte in the organic compound lining the column wall known as the stationary phase (assuming capillary GC)
- Allows specific compounds to be isolated from a mixture for quantification

Surface Acoustic Wave (SAW) Detectors—Theory of Operation

- Chemical coating
- Change in mass
- Analytes of interest—gases and VOCs

4100 Vapor Detector — Method Description

- Sample preparation - Direct Thermal Extraction Analysis
- Sample injection
- Chromatographic separation
- SAW detection

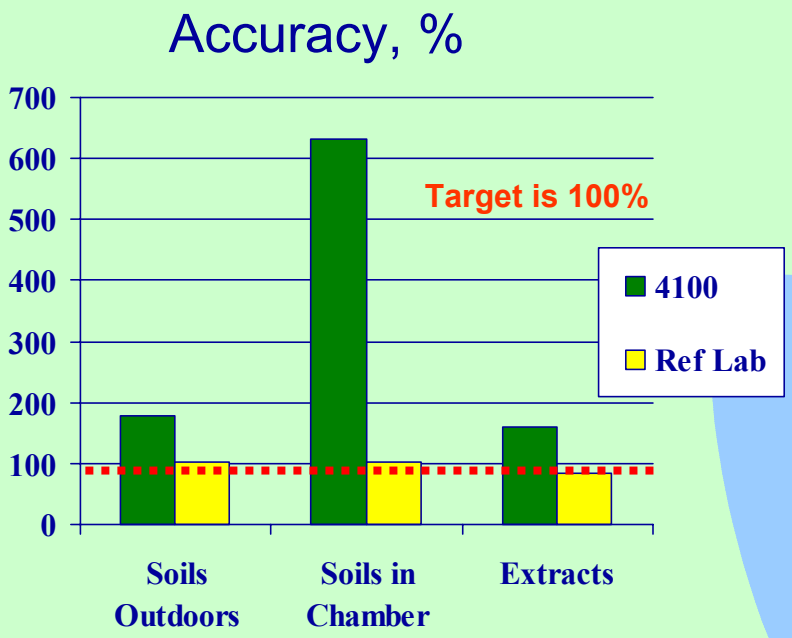
SAW Detector — Advantages

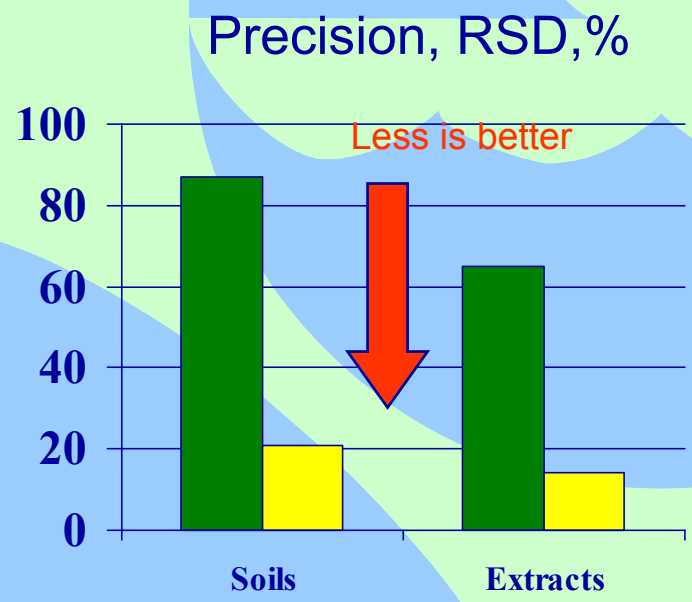
- Portability
- Increased selectivity

SAW Detector — Limitations

- Detector response is affected by:
  - Temperature
  - Humidity effect
- Non-specific response
- Detector saturation

EST
4100 Vapor Detector





EST
4100 Vapor Detector

Comparability: $R^2 = 0.177$ (soils); $R^2 = 0.187$ (extracts)

False positive results: 100% (8 of 8 soils); 38% (3 of 8 extracts)

False negative results: 5% (10 of 192 soils); 0% (0 of 16 extracts)

Detection limits: 26 ppm / 62 ppm (outdoor / chamber)

Throughput (2 analysts): 5-6 samples/h (outdoor)
10 samples/h (chamber)

4100 Vapor Detector (GS/SAW) — Electronic Sensor Technology

Regulatory levels		50 ppm	100 µg/100 cm^2
	RSD (precision)	72%	65%
	Percent recovery (accuracy)	132% (variably biased)	161% (consistently high)
Data quality	Imprecise and biased		

Ion-Specific Electrode-Based Chemical Analyzers — Theory of Application

- PCB screening kits for oil, soil, and wipe samples
- Extract PCBs from oil, soil, or wipe samples
- Convert PCBs to chloride
- Measure with chloride-specific electrode (quantitative)

Ion-Specific Electrode-Based Chemical Sensors — Method Description

- Weigh sample
- Solvent extraction of PCB
- Strip chloride from biphenyl
- Quench reaction
- Measure chloride ion potential
- Convert to PCB concentration

Ion-Specific Electrode-Based Chemical Analyzers — Advantages

- Portability
- Ease of operation
- Relatively high sample throughput

Ion-Specific Electrode-Based Chemical Analyzers — Limitations

- Potential interferences
- Varying response for different Aroclors

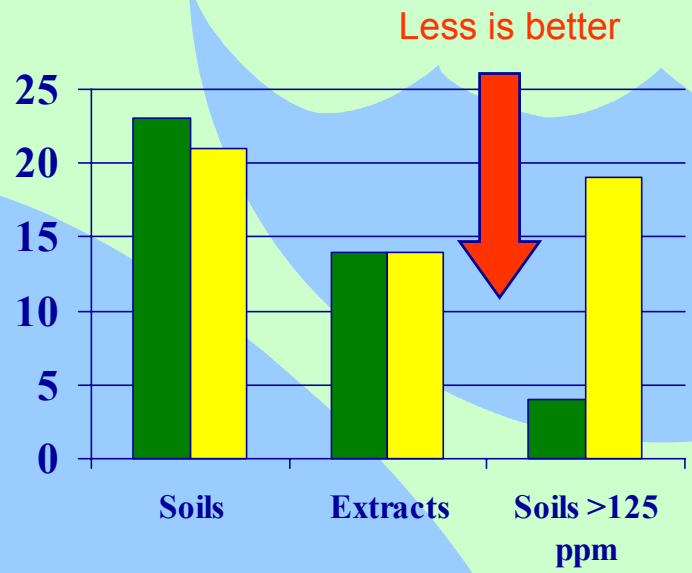
L2000 PCB/Chloride Analyzer — Dexsil Corporation

Detection limits	2 ppm based on PE analyses	
Throughput	10 samples per hour (chamber) by two operators	
	5 samples per hour (outdoors) by two operators	
Detection errors	Soil:	50% false positive (4 of 8)
		0% false negative (0 of 192)
	Extract:	50% false positive (4 of 8)
		0% false negative (0 of 16)

Dexsil
L2000 PCB/Chloride Analyzer

Accuracy, %

Precision, RSD,%



EPA

Dexsil
L2000 PCB/Chloride Analyzer

Comparability: $R^2 = 0.854$ (soils); $R^2 = 0.954$ (extracts)

False positive results: 50% (4 of 8 soils); 50% (4 of 8 extracts)

False negative results: 0% (0 of 192 soils); 0% (0 of 16 extracts)

Detection limits: 2 ppm

Throughput (2 analysts): 10 samples/h (chamber)
5 samples/h (outdoors)

L2000 PCB/Chloride Analyzer — Dexsil Corporation

Precision	All Soil:	L2000:	23%
		Laboratory:	21%
	Soils > 125 ppm	L2000:	4%
		Laboratory:	19%
	Extract:	L2000:	14%
		Laboratory:	14%
Accuracy	Soil:	208%	
	Extract:	149%	
Comparability		All samples	Samples 0 to 125 ppm
	Soils	R^2 = 0.854 (0 to 700 ppm)	R^2 = 0.781
	Extracts	R^2 = 0.954 (0 to 100 µg/mL)	not evaluated

L2000 PCB/Chloride Analyzer — Dexsil Corporation

Regulatory levels		50 ppm (soil)	100 µg/100 cm^2 (extract)
	RSD (precision)	12%	14%
	Percent recovery (accuracy)	147%	149%
Data quality	Precise and biased high		

Future ETV Site Characterization and Monitoring Technology Pilots

- 1998/99
  - Decision-support software (6)
  - Ground water sampling
  - Sediments sampling
  - TPH Test Kits
  - Geophysics
  - Explosives Test Kits

How Can States Participate?

- Design team
- Report evaluation
- Needs identification
- Vendor referrals

Links