

IMPLEMENTATION OF EPA METHOD 4025 (IMMUNOASSAY SCREENING) FOR DIOXIN SITE ASSESSMENT AND REMEDIATION

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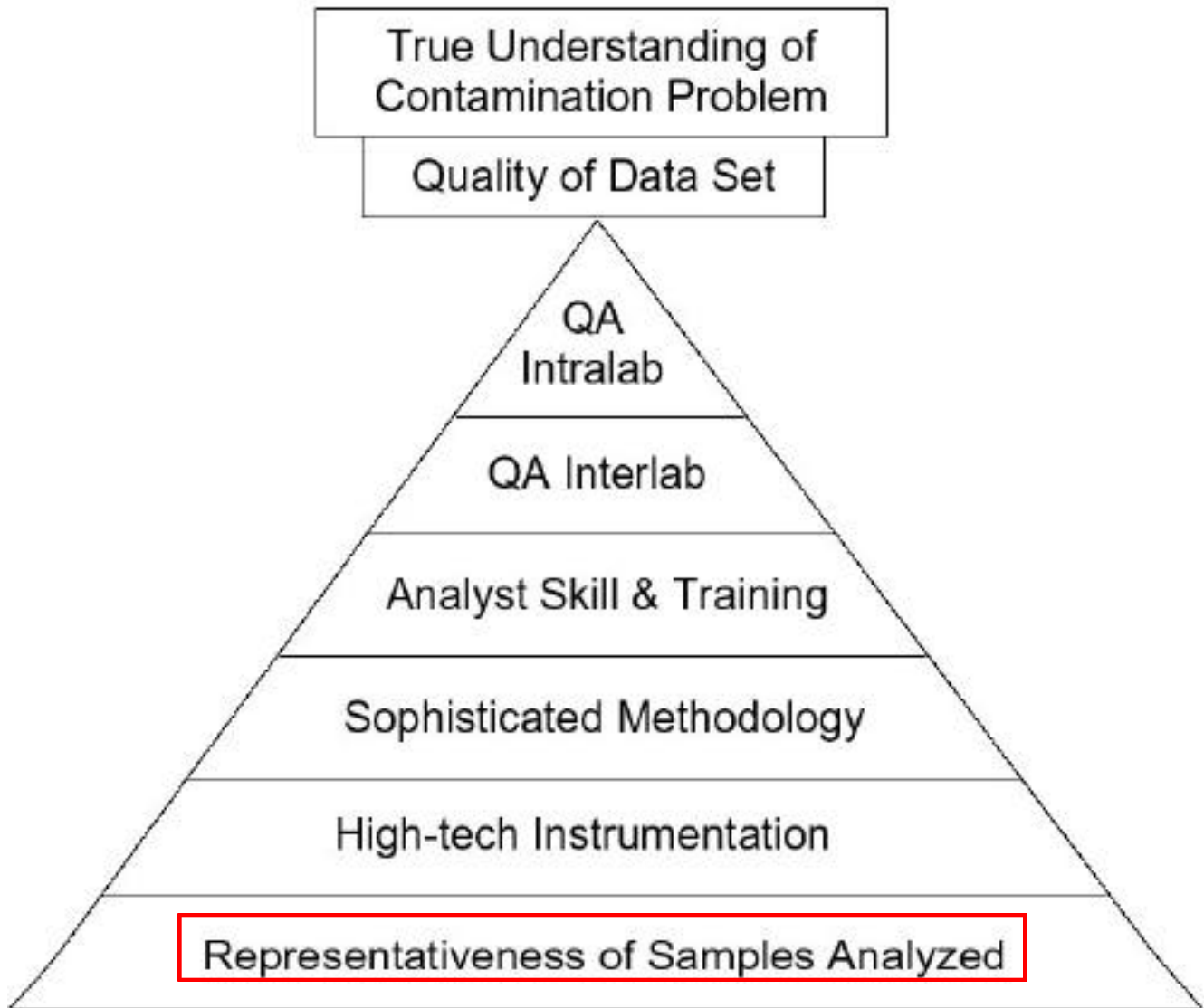
The Problem:

- ◆ Localized dioxin contamination at numerous sites around the world
- ◆ Persistence and bioaccumulation pose human and environmental health threat



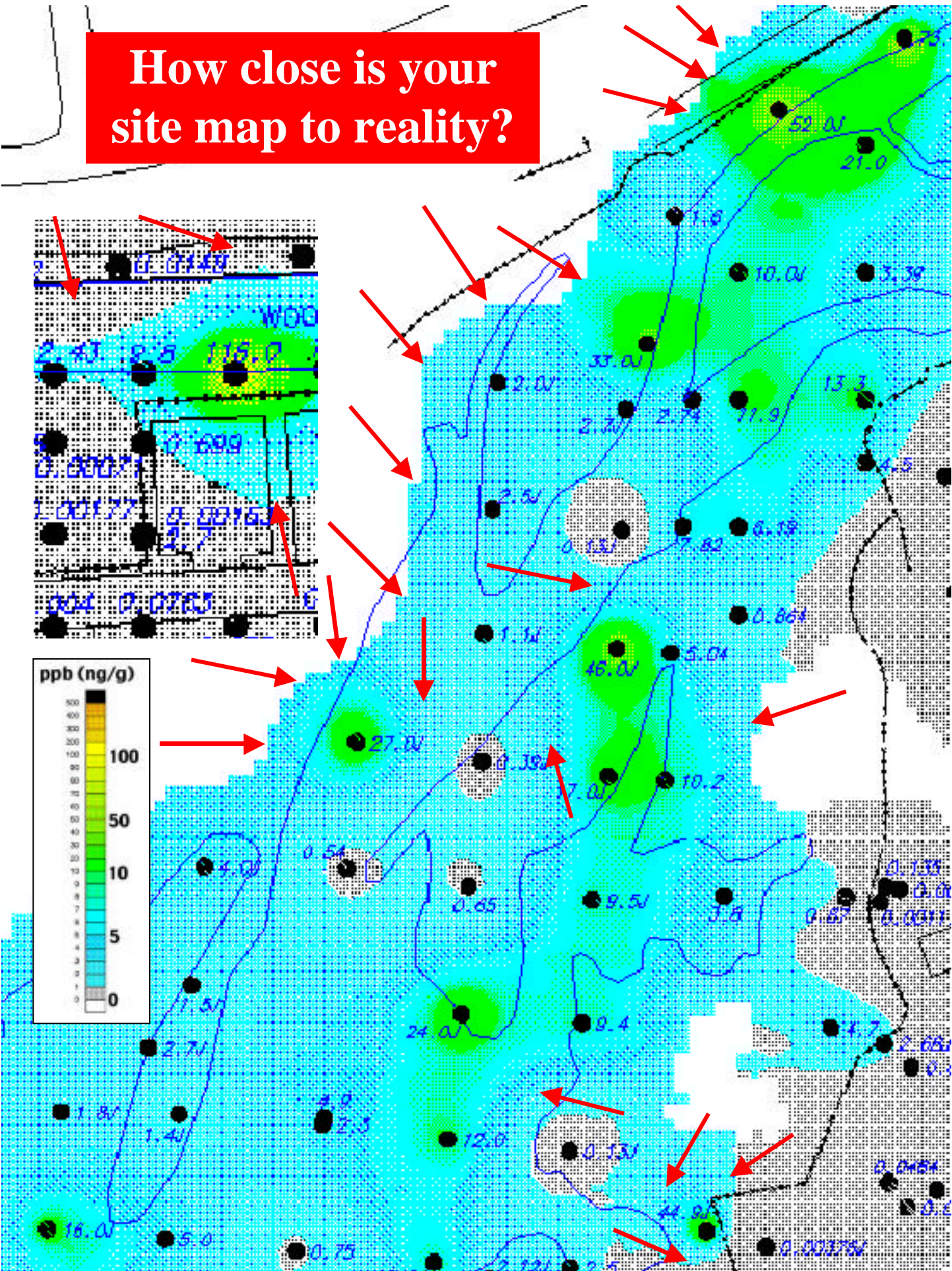
- ◆ Many concerns exist about inadequate site characterization and its effect on site assessment and remediation
- ◆ Cost, time, and difficulty of analysis are major barriers to adequate site characterization

The Foundation of the Problem:
Hierarchy of Factors Supporting
Environmental Decision-Making



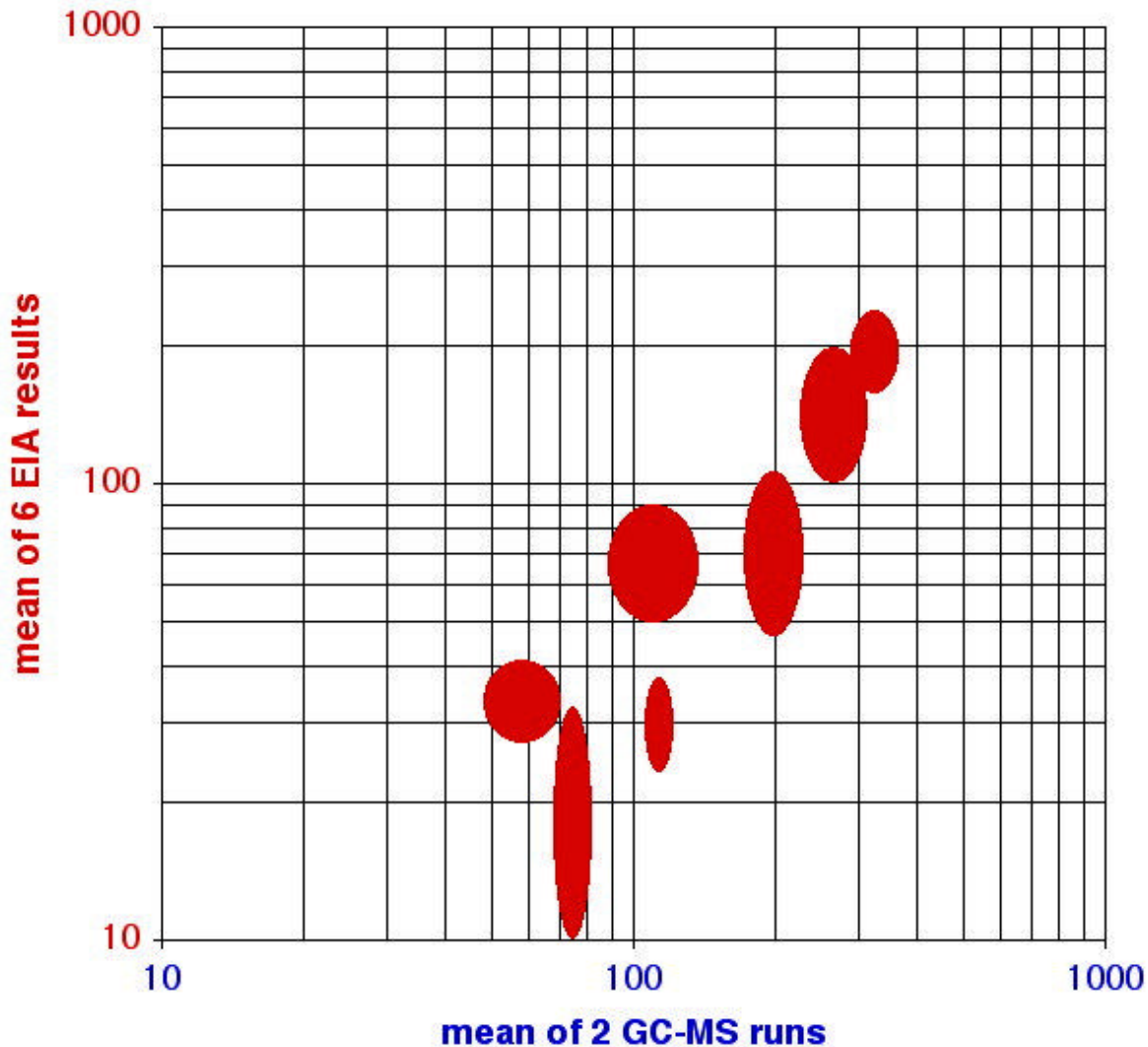
Statistically sound sampling is the foundation of everything else! If you don't have it, what do you have?

How close is your site map to reality?

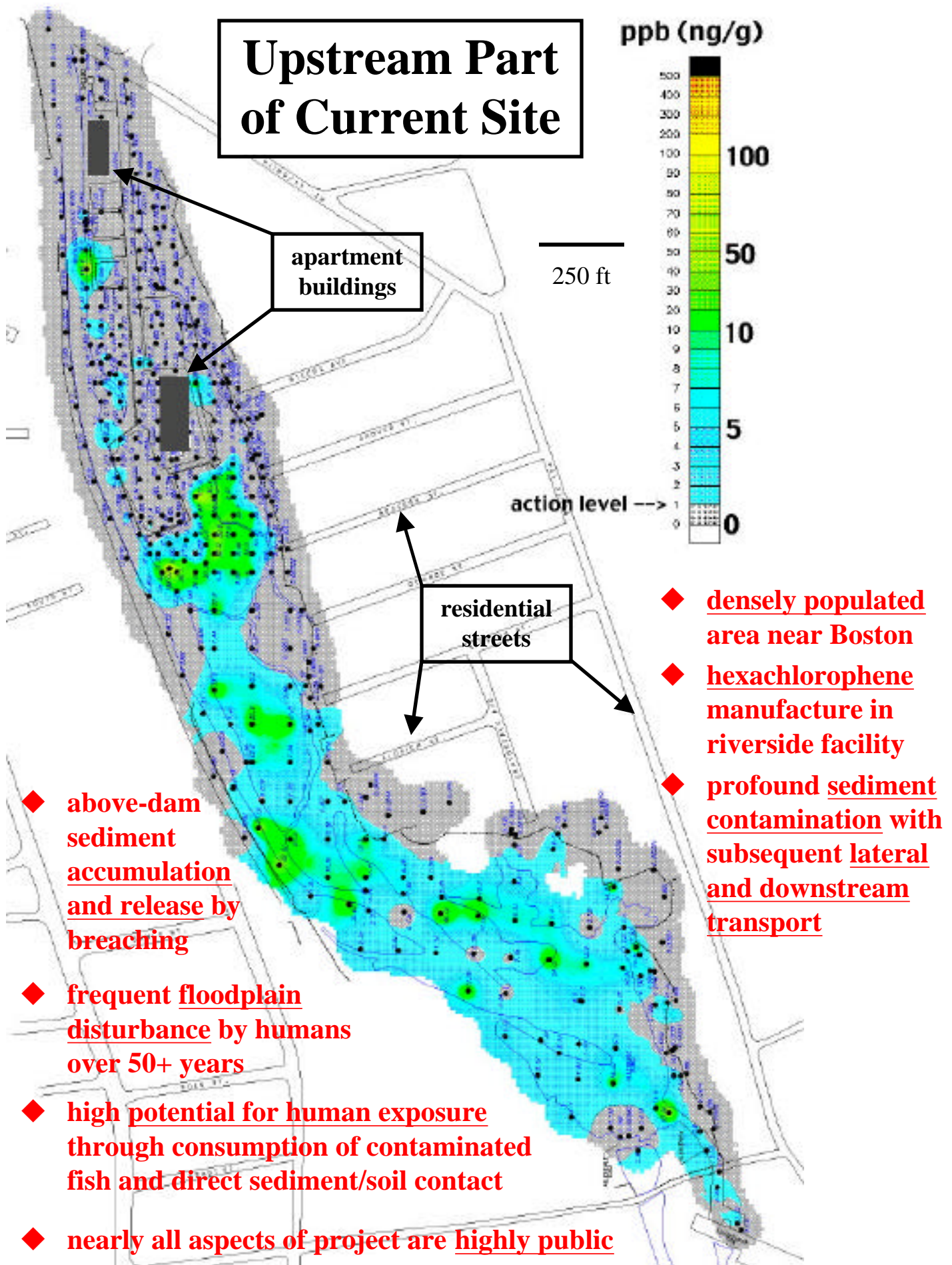


Remember that 8290 data show variation also

Correlation between EIA “screening” at 100 ppt and 8290 analysis (mean \pm SD) for 7 sewage sludge amended soils



- ◆ Statistically reliable estimates of 8290 precision require many (30 to >100) field duplicate pairs
- ◆ Sample heterogeneity is largest source of method variability
- ◆ Cost of 8290 analysis is the largest barrier to obtaining good data on overall method precision



Initial Site Characterization by Method 8290

- ◆ 11 discrete areas sampled along 2 to 3 km of river
- ◆ ~120 samples taken for Method 8290 analysis
- ◆ ~15-30 m grid spacing (some 5-10 m)
- ◆ samples mostly from near surface, few depth profiles done
- ◆ Method 8290 results gave wide range of concentrations up to approx. 150 ppb
- ◆ concentrations did not correlate strongly with depth; at least one deep sample (8 ft) was over 10 ppb

Actions Based on Initial Site Characterization

- ◆ fencing of drained pond to limit human exposure
- ◆ warning signs
- ◆ first pond dam reconstructed and pond refilled to reduce potential for direct human exposure
- ◆ determination of 1000 ppt TEQ target level for remediation
- ◆ identification of several areas for excavation and disposal (based on 8290 data) planned for spring/summer 2002
- ◆ Method 4025 analysis program to confirm “delineation” for removal action

Summary of Method 4025 Implementation Process

- ◆ Driven by EPA Region I
- ◆ Learn about new technology
- ◆ Generate trial data set using samples from site to be analyzed
- ◆ Make decision to integrate method into project
- ◆ Plan sampling and analysis
- ◆ Decide on QA to be used
- ◆ Set up lab and train analyst(s)
- ◆ Receive samples, prepare, and analyze
- ◆ Evaluate sample data and feed back into sampling program
- ◆ Evaluate QA data and feed back into analysis program
- ◆ Apply immunoassay data to site action plan
- ◆ Evaluate effectiveness of new technology

Method 4025

Implementation Process

◆ Driven by EPA Region I

EPA Region I saw real need for high spatial density and timely data in implementation of TRIAD approach

Years of experience with other 4000 series methods

Prior 4025 experience in validation process

Based in part on field lab trial at Region I lab

◆ Learn about new technology

Seminars, phone discussions, technical literature, demo

Review 4025 validation data package

◆ Generate trial data set using samples from site to be analyzed

For this site, is already incorporated into 4025 submission

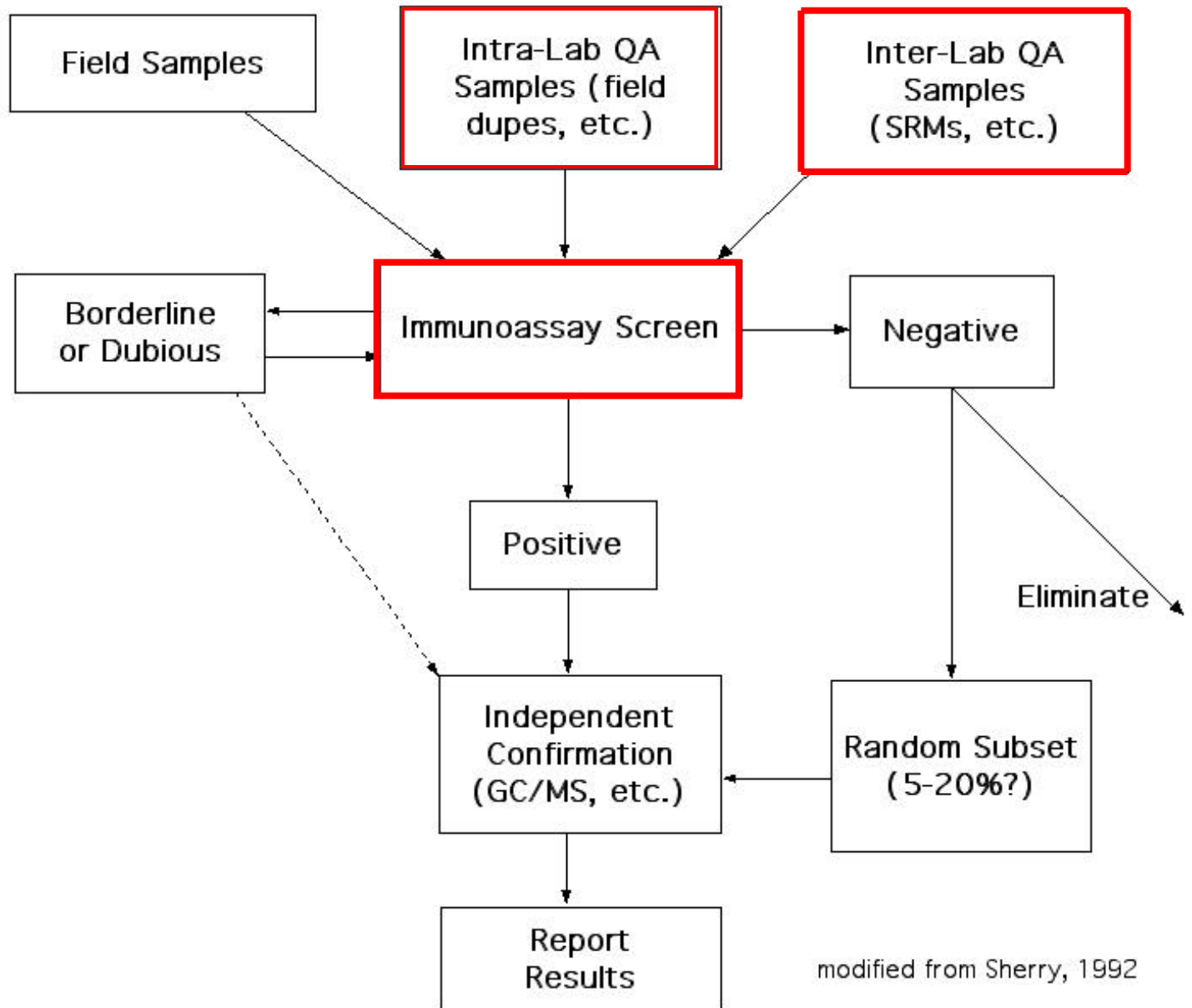
Many users demand data set with their own samples

This has value for training, calibration, user confidence

◆ Make decision to integrate method into project

Method 4025 should complement 8290, NOT replace it

Immunoassay Screening Strategy



Method 4025 should be just another tool in your analytical toolbox

Method 4025

Implementation Process

◆ Plan sampling and analysis

analysis to be done by engineering firm's lab

take samples mostly on 3 m grid at 3 to 5 depth ranges

transport samples daily from site to lab (100 km)

screening to be done at 500 ppt (2x "safety" factor)

sampling plan to be dynamic- adaptive in response to data

◆ Decide on QA to be used

Anything used for conventional methods is acceptable
except for surrogates or mass-labeled internal
standards

Within Method 4025-

standards with each run, calculated curve values
replicates

method blanks and oxidation blanks (+/- spike)

reference samples as solids or archived extracts

low ppt reference sample spiked at 0.5x and 2x
decision level (per 4025 validation package)

GC/MS based-

analyze subset by 8290 to confirm correlation and
calibrate EIA

Method 4025

Implementation Process

◆ Set up lab and train analyst(s)

CAPE assisted with lab setup

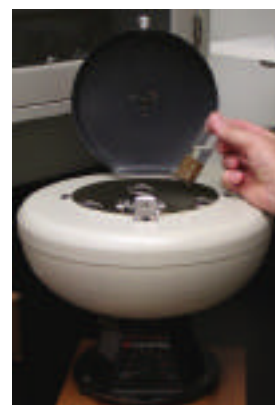
Minimal capital expenditure- **non-disposable items**
specific to Method 4025 **cost < \$3000**

CAPE **trained 2 chemists** inexperienced with 4000 series
methods, but accustomed to VOC analysis by
Photovac GC

Small time requirement for **training- 2 days on site**, hands
on with performance evaluation samples



**Facility and
Sample Prep
Equipment
Used for
Method 4025**



**Kits and
Equipment
Used for
Immunoassay
Portion of
Method 4025**



SP1
Sample
Prep Kit



Positive displacement
pipettors



Repeater Pipettor

DF1 Dioxin/Furan
Immunoassay Kit



Differential
Photometer



Method 4025

Implementation Process

- ◆ Receive samples, prepare, and analyze
 - samples collected AM, arrived at lab PM
 - extract and start EIA same day
 - approx. 20 samples/batch, 2 batches possible, max 40/day
 - finish EIA next morning for 24 hour turnaround
 - screen more than 1100 samples in 2 months
- ◆ Evaluate sample data and feed back into sampling program
 - 4025 data emailed daily to project manager and plotted on Action Area-specific site maps
 - continuous feed of 4025 data into conceptual site model and testing of model
 - weekly review of 4025 data with regulators
 - adaptive sampling plan- 4025 data used to rapidly and efficiently guide characterization efforts (critical part of TRIAD approach)
 - focus on filling data gaps in delineation of the extent of contamination

Method 4025

Implementation Process

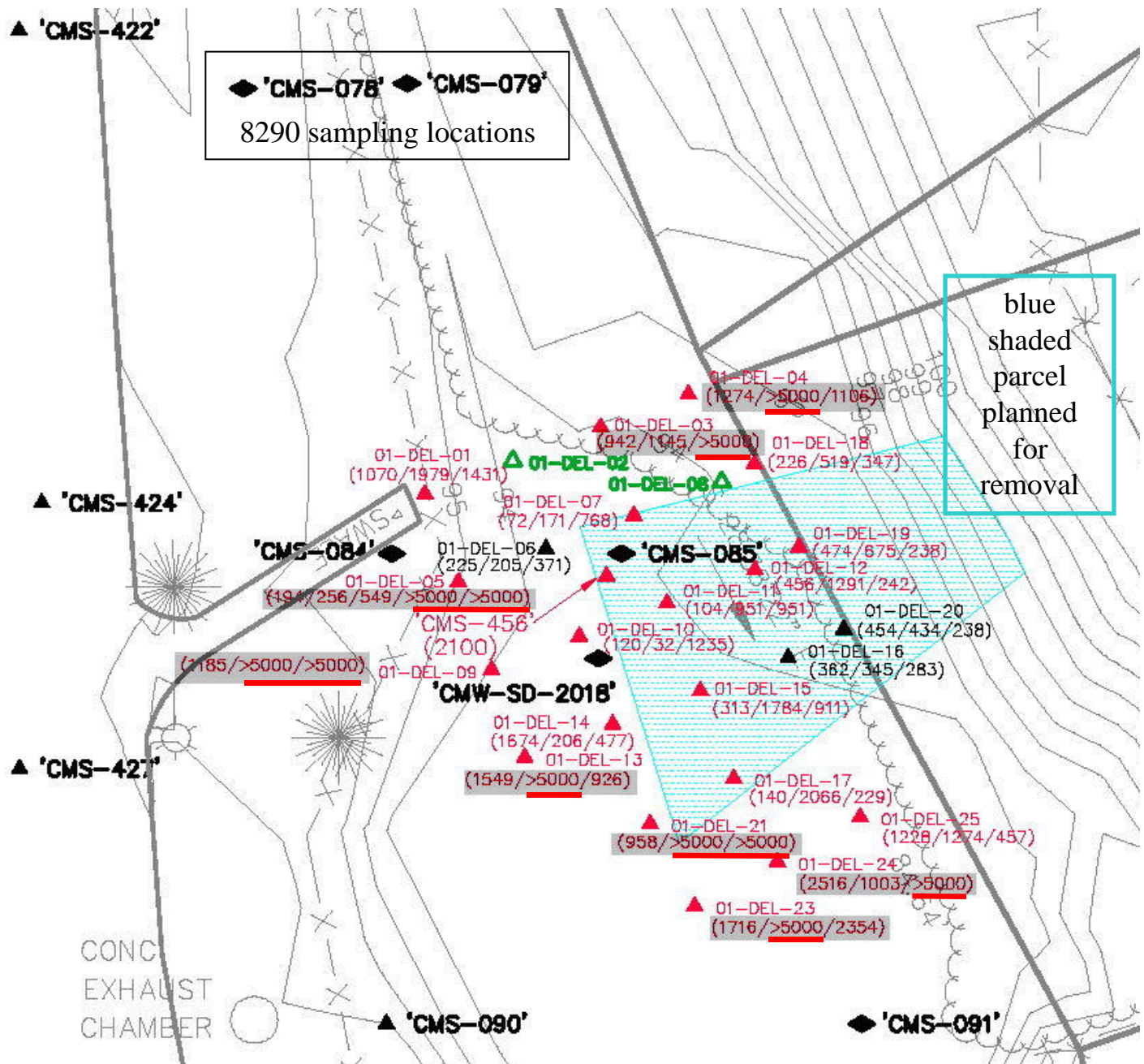
- ◆ Evaluate QA data and feed back into analysis program
 - within 4025 method- adequate after learning curve
 - GC/MS- only 4 samples analyzed by 8290 (all agree with 4025 semiquantitative decision at 500 ppt)
 - review and modify QA within 4025 method as needed
 - expand 4025 vs. 8290 comparison data set using as wide a range of concentrations as possible
 - goal is to maximize confidence in 4025-based decisions at 500 ppt target level
 - ongoing evaluation and improvement of data reliability is crucial for project success

Method 4025 Implementation Process- Summary of Method 4025 Results

- ◆ high frequency of samples over 500 ppt target level (>30% in some areas)
- ◆ many samples over 5000 ppt (>5% in one area)
- ◆ majority of highest samples clustered in 2 areas nearest original hexachlorophene source
- ◆ many high samples would have been missed using only earlier 8290 sampling grid
- ◆ positive results tended to be clustered- few sampling locations had only 1 sample (of 3 depths taken) over 500 ppt; most locations had 0, 2, or 3 positives

Area 1 central section

Method 4025 and 8290 sampling points and results



▲ 4025 sampling location and data

(depths in inches = 0-6/ 6-12/12-24/24-36/ 36-48)

Black indicates all samples at location are under 500 ppt.

Red indicates at least one sample at location is over 500 ppt.

Red underline indicates individual sample over 5000 ppt.

Method 4025 Implementation Process- Initial Conclusions from Immunoassay Results

- ◆ confirmed scrambled depth horizons due to both human activities and storm events
- ◆ gross distribution pattern conforms to expectations based on site history & geography
- ◆ prior 8290 analysis was insufficient to delineate the extent of dioxin contamination
- ◆ greater extent of contamination than previously thought

Method 4025

Implementation Process

◆ Apply immunoassay data to site action plan

EPA decision to delay planned removal action until extent of contamination is better delineated

increase number of 8290 comparison samples to support method correlation and provide better 4025 calibration

possible new round of 4025 analysis to further delineate extent of contamination

potential for revision of conceptual site model based on large quantity of new data

Method 4025

Implementation Process

◆ Evaluate effectiveness of new technology

Cost analysis-

\$125 per sample total for 4025, including labor (\$75 per sample for 4025 consumables)

potential large expansion of removal action

Benefits already realized-

huge increase in number of samples analyzed

reduction in field mobilizations for sampling

reduction in unnecessary 8290 samples

faster delineation effort from dynamic process

more focused sampling and analysis program which is more easily managed

Benefits anticipated but not yet realized-

reduction in field mobilizations for removal

reduction in number of 8290 samples for closure

high confidence in completeness of removal

Lessons learned and modifications required

more aggressive and comprehensive QA

focus on better reliability and defensibility of data

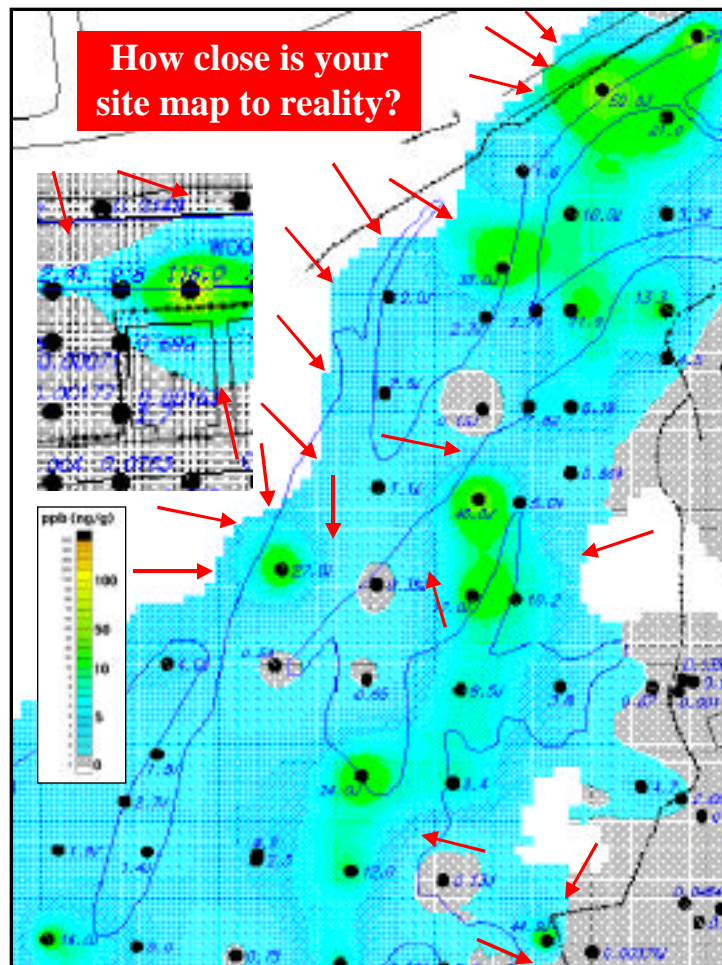
better integration of screening methods into dynamic process

Method 4025

Implementation Process-

Broad Conclusions

Rapid turnaround time allows multiple short cycles of sampling/analysis/decision for fast and effective site mapping (days or weeks rather than weeks or months)

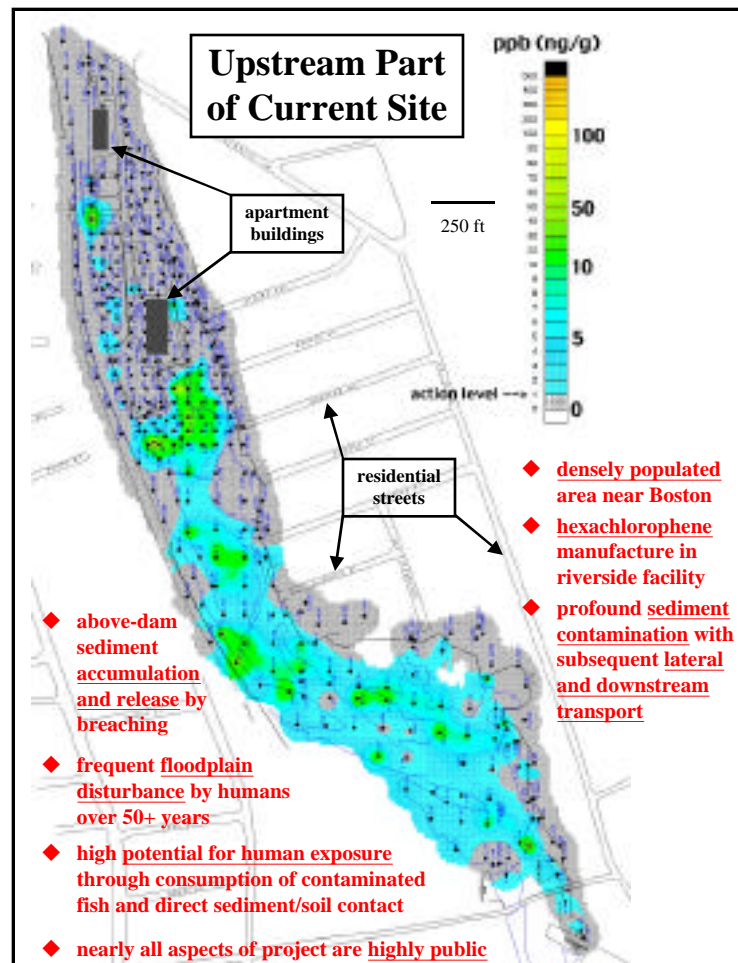


Method 4025

Implementation Process-

Broad Conclusions

Low cost per sample allows dramatically higher spatial resolution site mapping at the same cost as using Method 8290 alone



Method 4025

Implementation Process-

Broad Conclusions

Rapid turnaround time allows real time decision making during remediation actions (dramatically reduced heavy equipment mobilization/demobilization costs)



Method 4025

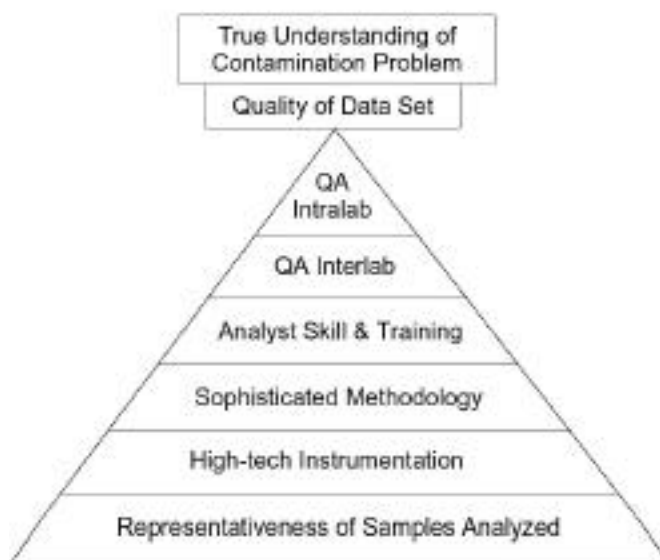
Implementation Process-

Broad Conclusions

Low cost per sample allows for dramatic improvement in statistical reliability of the final data set.

The Foundation of the Problem:

Hierarchy of Factors Supporting
Environmental Decision-Making



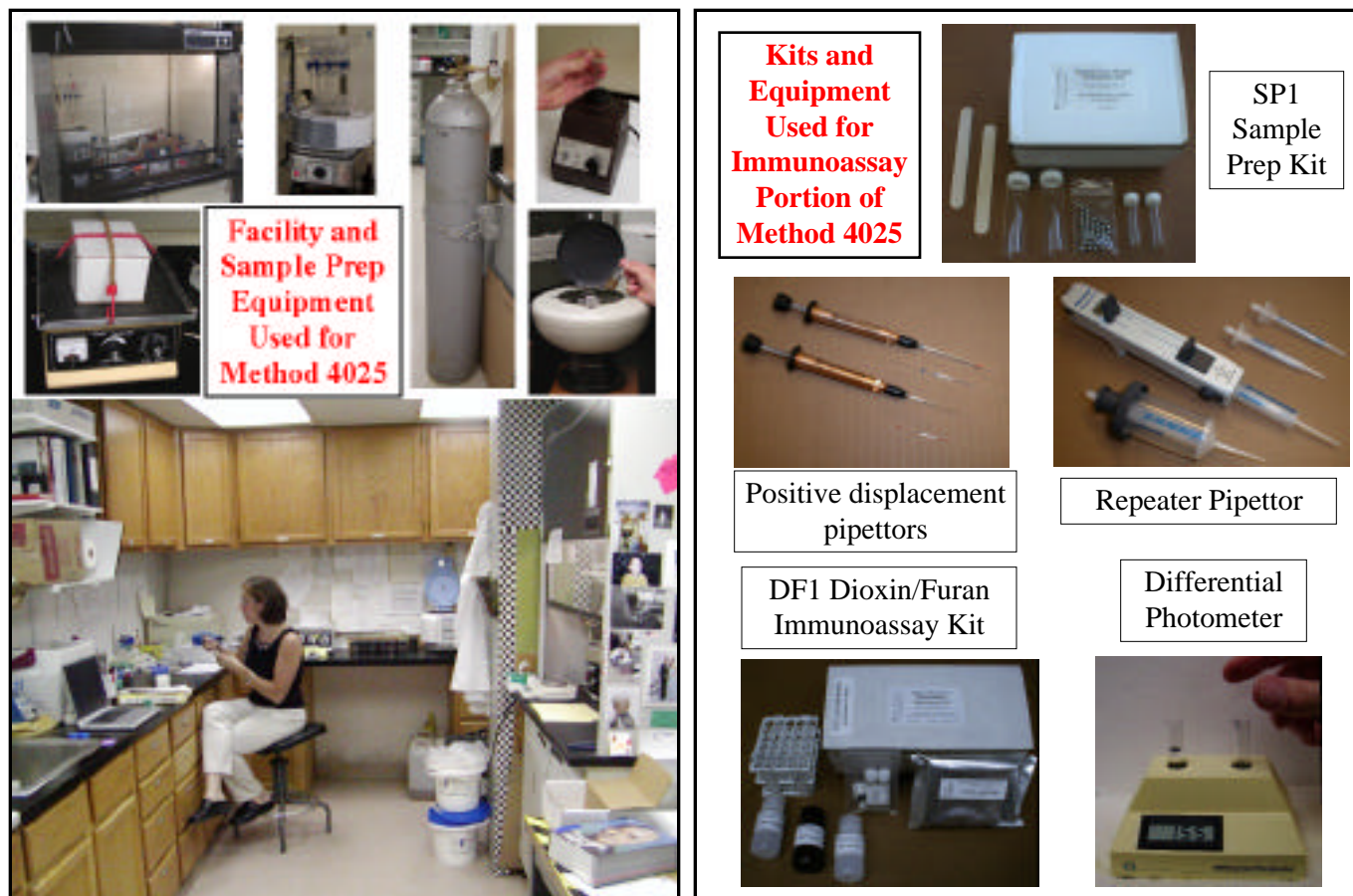
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Method 4025

Implementation Process-

Broad Conclusions

The use of screening methods such as Method 4025 has the potential to introduce large and qualitative changes in the way dioxin sites are handled (TRIAD approach), just as seen a decade ago for other 4000 series methods



**Novel technologies like this
will help us make progress
toward our common goal of a
safe and clean environment.**

