Bias in Organochlorine Pesticide Data: Comparison of Analyses by GC/ECD and HRGC/MS/MS

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Outline

- Purpose of Investigation
- Sampling and Analytical Methods
- Analytical Results (or Anomalies?)
- Potential Impact on Data Usability
- How can we do better?
- Conclusion
- Q & A

Once you have knowledge of something, you simply cannot not do something about it, because to do otherwise is…

Purpose of Investigation

Identify if Chemicals of Interest may be present

Do we really know what's out there?

Project Objectives

- Conduct sediment investigations in urban/ industrial setting
- Identify if COIs may be present
- Delineate nature and extent
- Use data to support potential remedial decisions
- Source tracing

Overview of Sampling and Analysis

Sample Design and Method Selection

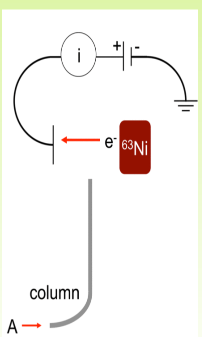
Overall, uncertainty is often attributable to where & how samples are collected, the matrix (heterogeneity matters), and the analytical methods used

Summary Sampling and Analysis

- Samples collected included:
  - Surface (grab) sediment samples
  - Subsurface (core) sediment samples
  - Sediment trap samples (collected quarterly)
  - Soil bank and debris samples
- COI’s included PCBs, OC Pesticides, PHCs, PCDD/Fs, SVOCs, PAHs, and more

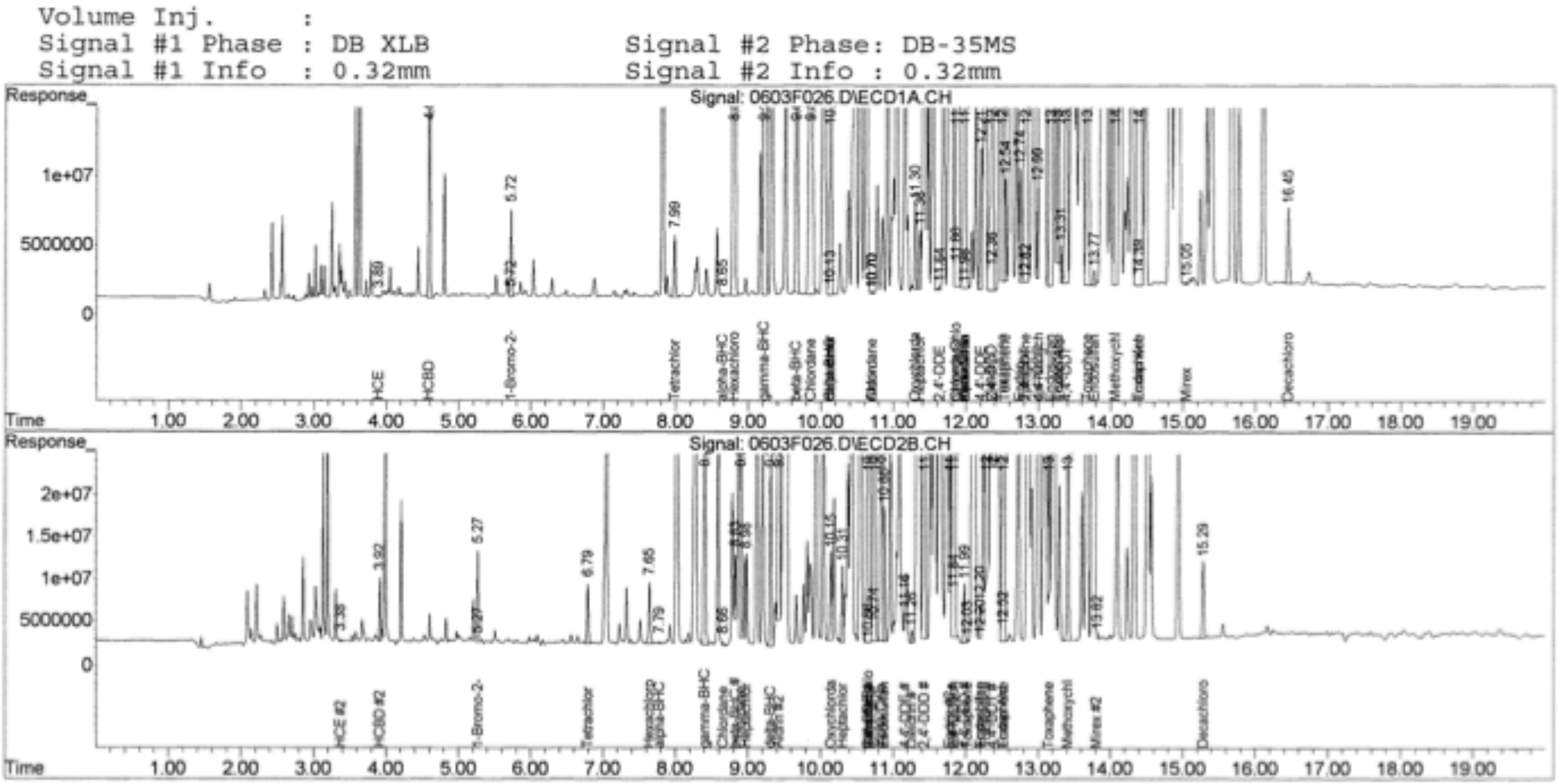
Sampling and Analysis, cont.

- GC/ECD method:
  - Routinely used in labs, relatively inexpensive
  - Good sensitivity with relatively clean extracts
  - Historically used to compare data sets
  - Suffers from well-documented limitations:
    - Interferences (co-extracted non-target compounds)
    - Often elevated RLs & false negatives/positives



http://en.wikipedia.org/wiki/Electron_capture_detector

GC/ECD Chromatogram of Core Sample C3 for Organochlorine Pesticides



- Laboratory reported only 3 of 32 OC pesticides as detected: gamma-Chlordane at 190 *PD* ug/kg, Endrin at 5.7 *P* ug/kg, and 2,4'-DDD at 250 *D*, ug/kg (analysis at 1x and 50x dil.). Analysis by HRGC/MS/MS reported 9 of 31 OC pesticides as detected. A1260 reported at 6,500 ug/Kg in this sample

P = percent difference >40 percent between concentrations quantified on dual columns D = Dilution

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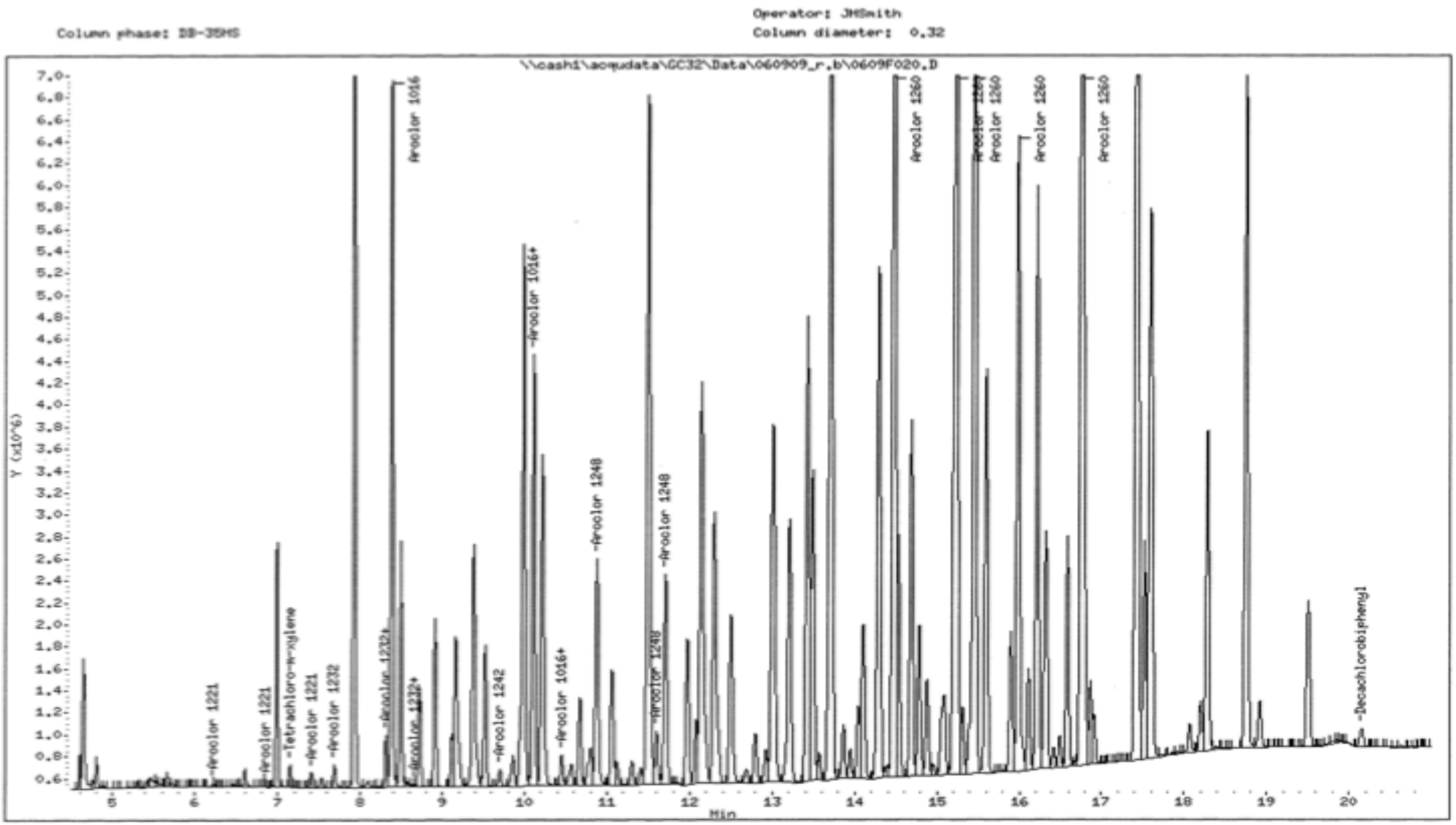
GC/ECD Chromatogram of Core Sample C3 for PCBs (DB-35MS column only)



• Laboratory reported A1260 reported at 6,500 ug/kg (dual column result at 5,300 ug/kg). Analysis at 50x dilution.

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Sampling and Analysis, cont.

- Confirmatory analyses by HRGC/MS/MS:
  - Elevated detections and high RLs by GC/ECD
  - Used archived samples (stored frozen at -20°C); holding times slightly >1 yr.
  - Most background noise and interferences 'filtered' due to tandem MS and MRM

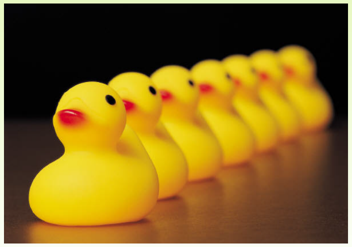
Basically, parent ion goes through first quadrapole; fragmented in collision cell; product ion goes through second quadrapole and other non-target ions are filtered out

Sampling and Analysis, cont.

- HRGC/MS/MS, cont.:
  - Acquire unique spectral 'fingerprints'
  - More definitive analyte identification
  - Use of isotopically-labeled standards increases precision and accuracy
  - Achieve detection levels up to 20 times lower (or more) than typically achieved by GC/ECD
  - Overall, greater sensitivity and selectivity

Sampling and Analysis, cont.

- Reviewed and evaluated all data:
  - 100-percent data verification and validation
  - Evaluated "chemical fingerprint"



Make sure all the "ducks" are in a row!

Analytical Results (or Anomalies?)

My data are usable, right?

Well, maybe yes, or no,
or I am not sure?

Not using most appropriate analytical method
may result in biased results and incorrect interpretation

Comparison of Results

	Sediment Subsurface (Core) Samples (ug/kg dry wt.)						
Constituent	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
2,4'-DDT (GC/ECD)	5.1 U	12 U	120 U	52 U	0.58 U	3.1 U	9.6 U
2,4'-DDT (HRGC/MS/MS)	0.0060 U	0.0060 U	0.0060 U	0.0060 U	0.0060 U	0.0060 U	3.4
% Difference	*	*	*	*	*	*	*
2,4'-DDD (GC/ECD)	10	30	230	80	25	6.3	19 J
2,4'-DDD (HRGC/MS/MS)	12	14	3.3	3.1	2.9	0.23	17
% Difference	-20.0	53.3	98.6	96.1	88.4	96.3	(ok)
2,4'-DDE (GC/ECD)	0.27 U	0.50 U	0.25 U	0.33 U	0.16 U	2.2 U	0.3 U
2,4'-DDE (HRGC/MS/MS)	0.35 J	0.66	0.75 J	0.43	0.26	0.0069 U	0.43
% Difference	(ok)	(ok)	(ok)	(ok)	(ok)	*	(ok)

1. **100% of 2,4'-DDT by GC/ECD are RLs of 97 to 20,000 times greater than HRGC/MS/MS.**
2. **71% of 2,4'-DDD results by GC/ECD are 1 to 70 times greater than HRGC/MS/MS for detects.**
3. **2,4'-DDE results are comparable, with one RL at 320 times greater than HRGC/MS/MS.**

Comparison of Results, cont.

	Surface Sediment (Grab) Samples (ug/kg, dry wt.)							
Constituent	**G1**	**G2**	**G3**	**G4**	**G5**	**G6**	**G7**	**G8**
2,4'-DDT (GC/ECD)	9.3 U	12 U	6.2 U	79	20	53 U	6.8 J	2.3 J
2,4'-DDT (HRGC/MS/MS)	0.0060 U	0.14 J	0.0060 U	0.0060 U	0.0069 J	0.06 U	0.06 U	0.086
% Difference	*	*	*	*	*	*	*	96.3
2,4'-DDD (GC/ECD)	22	17	13	20 U	7.1 U	120 J	3.4 U	0.97 U
2,4'-DDD (HRGC/MS/MS)	0.15 J	0.78	0.057 J	0.56	0.11	14	2.9	0.44
% Difference	99.3	95.4	99.6	*	*	*	(ok)	*
2,4'-DDE (GC/ECD)	0.062 U	0.18 U	2.0 U	17 U	0.2 U	63 U	1.2 U	0.58
2,4'-DDE (HRGC/MS/MS)	0.0069 U	0.13 J	0.0069 U	0.030 J	0.0094 J	0.18	0.14	0.03 J
% Difference	*	(ok)	*	*	*	*	*	94.8

1. **100% of 2,4’-DDT RLs/detects by GC/ECD are 27 to 13,200 times greater than HRGC/MS/MS RLs.**
2. **88% of 2,4’’-DDD results by GC/ECD show high bias (elevated RLs and/or detected concentrations).**
3. **88% of 2,4’-DDE results by GC/ECD show high bias (elevated RLs and/or detected concentrations).**

Comparison of Results, cont.

	Sediment Subsurface (Core) Samples (ug/kg dry wt.)						
Constituent	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
4,4'-DDT (GC/ECD)	29	49 U	150 U	180 U	28 U	5.7 U	440
4,4'-DDT (HRGC/MS/MS)	0.014 U	0.014 U	0.014 U	0.014 U	3.0	0.014 U	15
% Difference	*	*	*	*	*	*	96.6
4,4'-DDD (GC/ECD)	14	33	2.9 U	4.9 U	5.1	0.43 U	17
4,4'-DDD (HRGC/MS/MS)	28	35	12	9.7	18	0.51	31
% Difference	-100	-6.1	*	*	-253	(ok)	-82.4
4,4'-DDE (GC/ECD)	3.2 J	1.2 U	1.1 U	1.6 J	4.4 J	0.42 U	6.5 J
4,4'-DDE (HRGC/MS/MS)	2.4	6.7	9.3 J	5.6	5.0	0.13 J	6.3
% Difference	25.0 (ok)	*	*	-250	-13.6 (ok)	(ok)	(ok)

1. **100% of 4,4'-DDT results by GC/ECD have RLs of 410 to 12,900 times greater than HRGC/MS/MS. Two high detected concentrations by GC/ECD, but not supported by HRGC/MS/MS.**
2. **4,4'-DDD results by GC/ECD mixed; five results biased low (higher concentration by HRGC/MS/MS).**
3. **4,4'-DDE results by GC/ECD mixed; three results biased low (higher concentration by HRGC/MS/MS).**

Comparison of Results, cont.

	Surface Sediment (Grab) Samples (ug/kg, dry wt.)							
Constituent	**G1**	**G2**	**G3**	**G4**	**G5**	**G6**	**G7**	**G8**
4,4'-DDT (GC/ECD)	96	110 U	63 U	100	42	78 U	4.2	2.6
4,4'-DDT (HRGC/MS/MS)	0.014 U	1.9	0.097 J	0.59	0.044	0.51	1.4	0.52
% Difference	*	*	*	*	*	*	*	*
4,4'-DDD (GC/ECD)	0.37	1.5 U	0.15 U	1.1 U	8.3	24	8.2	2.9
4,4'-DDD (HRGC/MS/MS)	0.39	2.5	0.015 U	1.8	0.27	57	14	1.1
% Difference	(ok)	*	*	(ok)	*	-138	-71	62
4,4'-DDE (GC/ECD)	0.94 U	1.2 U	0.15 U	0.22	2.9 U	1.6 U	1.6 U	6.5 j
4,4'-DDE (HRGC/MS/MS)	0.33	2.7	0.27	0.79	0.19	1.7	1.7	6.3
% Difference	(ok)	*	*	*	*	(ok)	(ok)	(ok)

1. **100% of 4,4'-DDT results by GC/ECD have high RLs (3 to 6,900 times greater than HRGC/MS/MS results. Three high detected concentrations by GC/ECD, but not supported by HRGC/MS/MS.**
2. **4,4'-DDD results by GC/ECD mixed; three results biased high and three results biased low.**
3. **4,4'-DDE results by GC/ECD mixed; three results biased low and one result with higher RL.**

Comparison of Results, cont.

	Sediment Subsurface (Core) Samples (ug/kg dry wt.)						
Constituent	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
Σ 2,4' and 4,4'-DDx (GC/ECD)	56.2 J	63	230	81.6 J	34.5 J	6.3	483
Σ of 2,4' and 4,4'-DDx (HRGC/MS/MS)	42.8	56.4	25.4	18.8	29.2	0.87	73.1
% Difference	23.8 (ok)	10.5 (ok)	88.9	76.9	15.4 (ok)	86.2	84.9
Σ Chlordanes (GC/ECD)	9.2	47 J	180 J	63 J	14 J	10.2 J	7.3 J
Σ Chlordanes (HRGC/MS/MS)	0.068	0.36	0.82	0.986	2	0.065	8.3
% Difference	99.3	99.2	99.5	98.4	70.6	99.4	-13.7 (ok)
Σ PCBs (as Aroclors)	300	950	6,500	1,500	650	186	216
NWTPH-Dx (mg/kg)	5,700	5,800	1,500	1,010	1,010	96	1,500

1. **Σ 2,4' and 4,4'-DDx results by GC/ECD show positive bias in 4 of 7 samples with concentrations from 7 to 9 times greater than HRGC/MS/MS concentration.**
2. **90% of Σ Chlordane results by GC/ECD show positive bias with concentrations from 7 to 220 times greater than HRGC/MS/MS concentration.**
3. **Presence of PCBs (and PHCs?) biasing results? Non-target compounds likely interferences?**

Comparison of Results, cont.

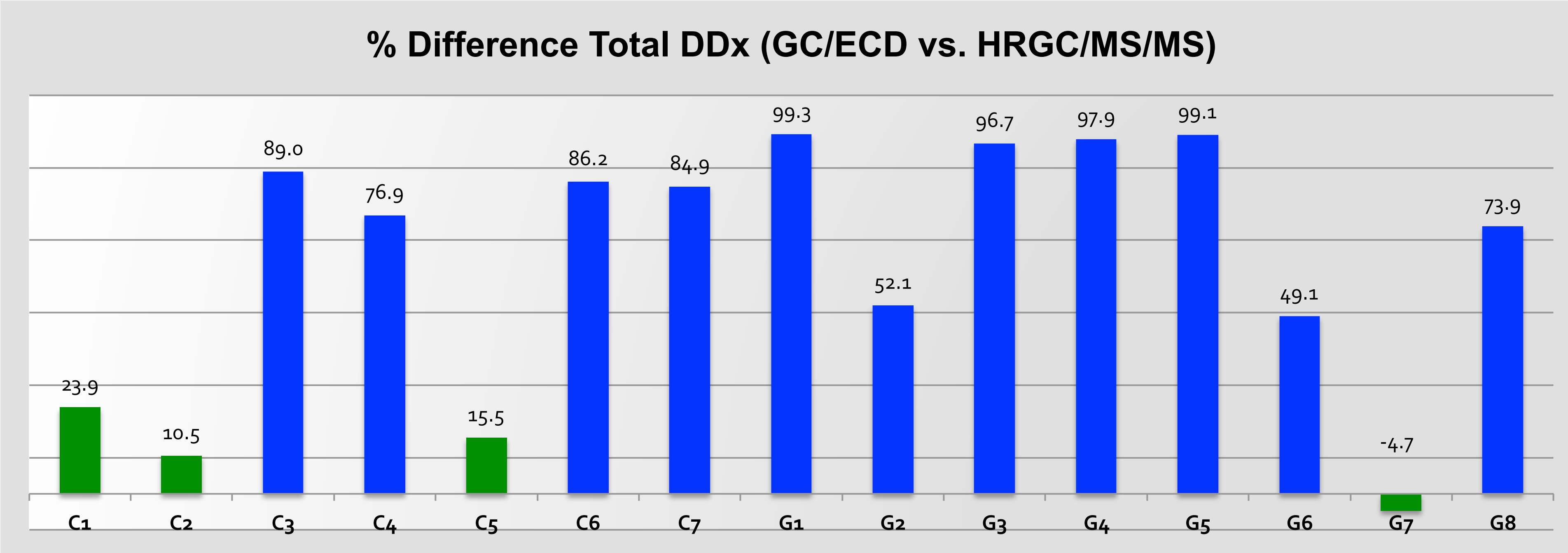
	Surface Sediment (Grab) Samples (ug/kg, dry wt.)							
Constituent	G1	G2	G3	G4	G5	G6	G7	G8
Σ 2,4' and 4,4'-DDx (GC/ECD)	118	17	13	179	70.3	144	19.2	11.1
Σ of 2,4' and 4,4'-DDx (HRGC/MS/MS)	0.87	8.15	0.42	3.77	0.63	73.3	20.1	2.9
% Difference	99.3	52.1 (ok)	96.8	97.9	99.1	49.1 (ok)	(ok)	73.4
Σ Chlordanes (GC/ECD)	23 J	97 U	54 U	46 J	15 J	4.3	6	1.9
Σ Chlordanes (HRGC/MS/MS)	0.359	0.83	0.262	0.702	0.25 J	2.0	15.6	1.05
% Difference	98.4	*	*	98.5	98.3	53.4 (ok)	-160	44.7 (ok)
Σ PCBs (as Aroclors)	960	1,400	2,000	1,300	520	4,200	260	49.8
NWTPH-Dx (mg./Kg)	no data	670	103	210	110	670	680	330

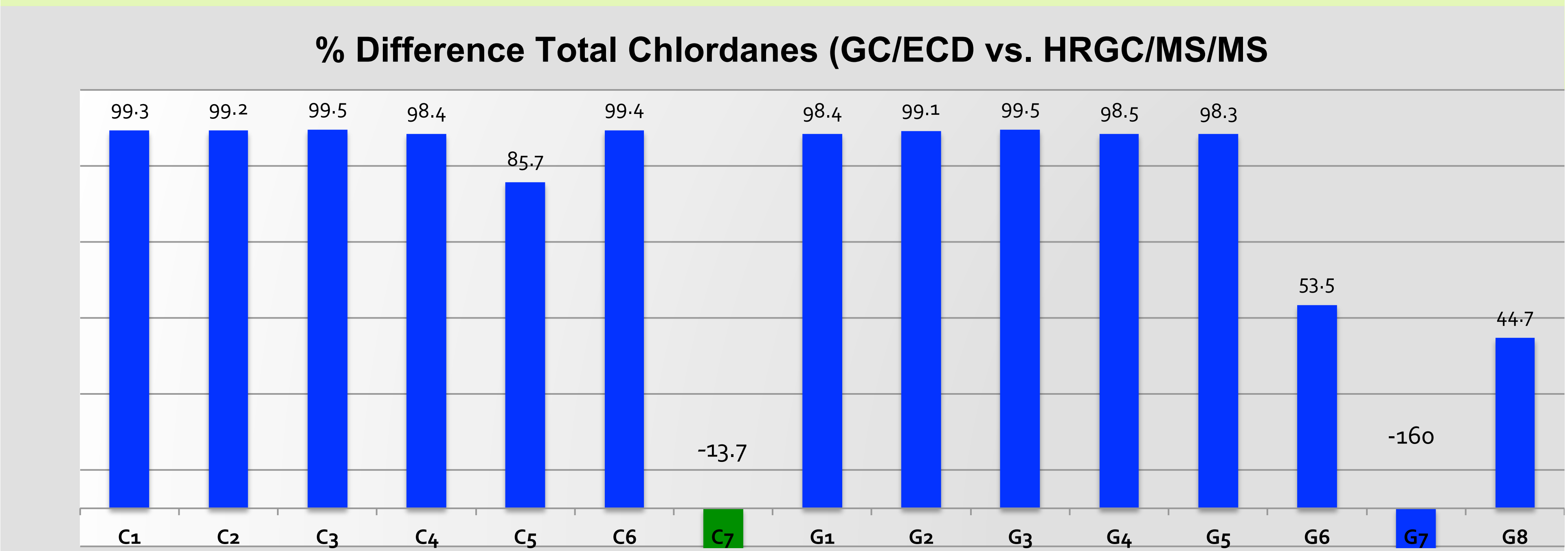
1. **63% of Σ 2,4’ and 4,4’-DDx results by GC/ECD show positive bias**
2. **63% of Σ Chlordane results by GC/ECD show positive bias; *cis*-nonachlor and trans-chlordane most dominant contributors to Σ Chlordane**
3. **Presence of PCBs (and PHCs?) biasing results? Non-target compounds likely interferences?**

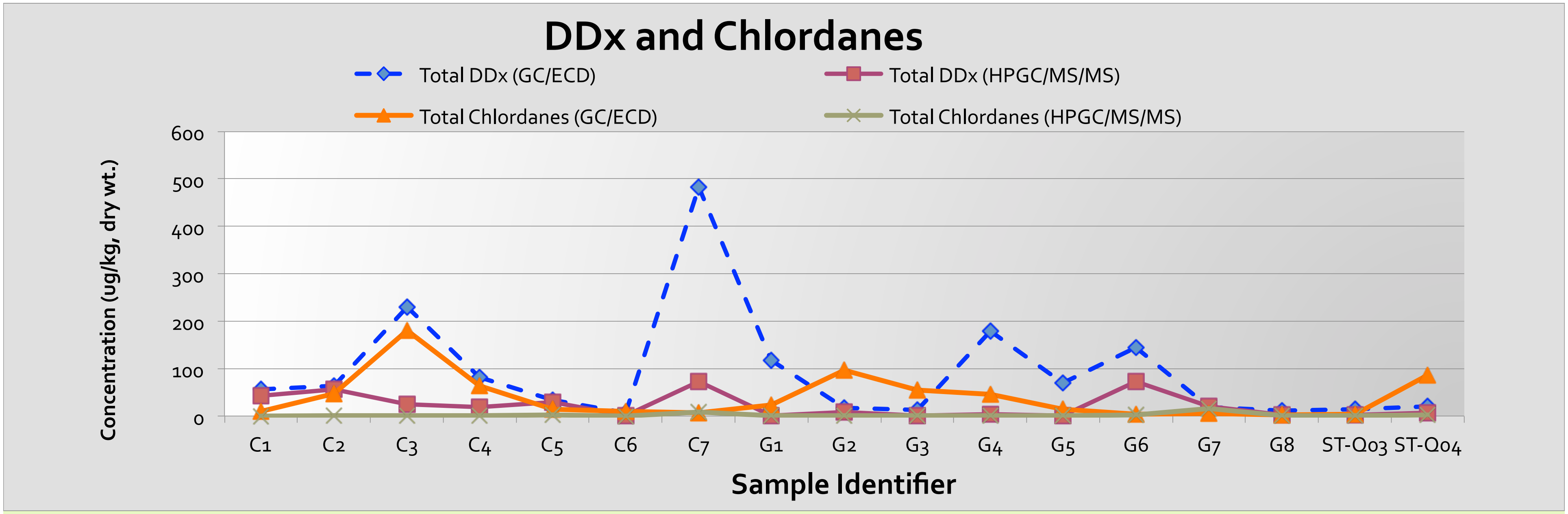
Comparison of Results, cont.

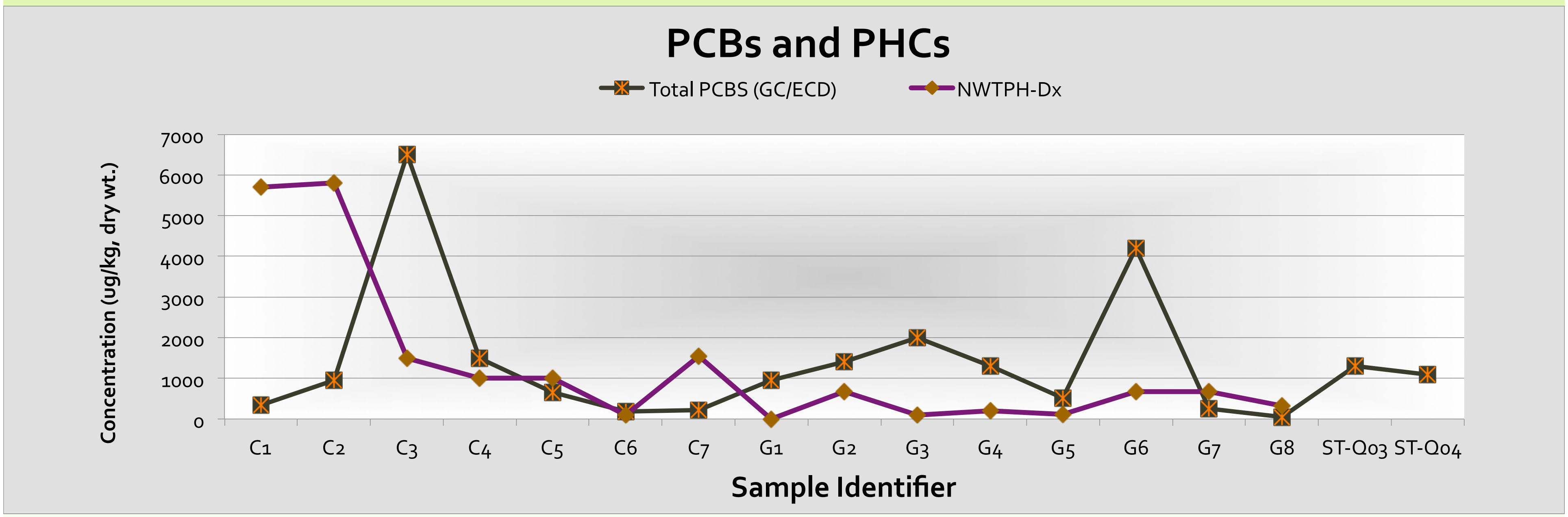
	Sediment Trap Samples (ug/kg, dry wt.)	
Constituent	ST-Q3	ST-Q4
Σ 2,4' and 4,4'-DDx (GC/ECD)	14	20.4
Σ of 2,4' and 4,4'-DDx (HRGC/MS/MS)	2.84	7.45
% Difference	79.7	63.5
Σ Chlordanes (GC/ECD)	4.3 U	86 U
Σ Chlordanes (HRGC/MS/MS)	0.655 J	2.5
% Difference	*	*
Σ PCBs (as Aroclors)	1,300	1,100
Σ PCBs (as sum of congeners)	549	72.2
% Difference	57.8	93.4

1. **Σ 2,4’ and 4,4’-DDx results by GC/ECD are 2.7 to 4.5 times greater than HRGC/MS/MS.**
2. **Σ Chlordane results by GC/ECD reported at RLs that are 6.7 to 34 percent greater than HRGC/MS/MS.**
3. **PCBs by GC/ECD are 2.4 to 15 times greater than by HRGC/HRMS.**


% Difference Total DDx (GC/ECD vs. HRGC/MS/MS)
23.9
10.5
89.0
76.9
15.5
86.2
84.9
99.3
52.1
96.7
97.9
99.1
49.1
-4.7
73.9
C1
C2
C3
C4
C5
C6
C7
G1
G2
G3
G4
G5
G6
G7
G8


% Difference Total Chlordanes (GC/ECD vs. HRGC/MS/MS
99.3
99.2
99.5
98.4
85.7
99.4
-13.7
98.4
99.1
99.5
98.5
98.3
53.5
-160
44.7
C1
C2
C3
C4
C5
C6
C7
G1
G2
G3
G4
G5
G6
G7
G8


DDx and Chlordanes
Total DDx (GC/ECD)
Total DDx (HPGC/MS/MS)
Total Chlordanes (GC/ECD)
Total Chlordanes (HPGC/MS/MS)
Concentration (ug/kg, dry wt.)
600
500
400
300
200
100
0
C1
C2
C3
C4
C5
C6
C7
G1
G2
G3
G4
G5
G6
G7
G8
ST-Q03
ST-Q04
Sample Identifier


PCBs and PHCs
Total PCBS (GC/ECD)
NWTPH-Dx
Concentration (ug/kg, dry wt.)
7000
6000
5000
4000
3000
2000
1000
0
C1
C2
C3
C4
C5
C6
C7
G1
G2
G3
G4
G5
G6
G7
G8
ST-Q03
ST-Q04
Sample Identifier

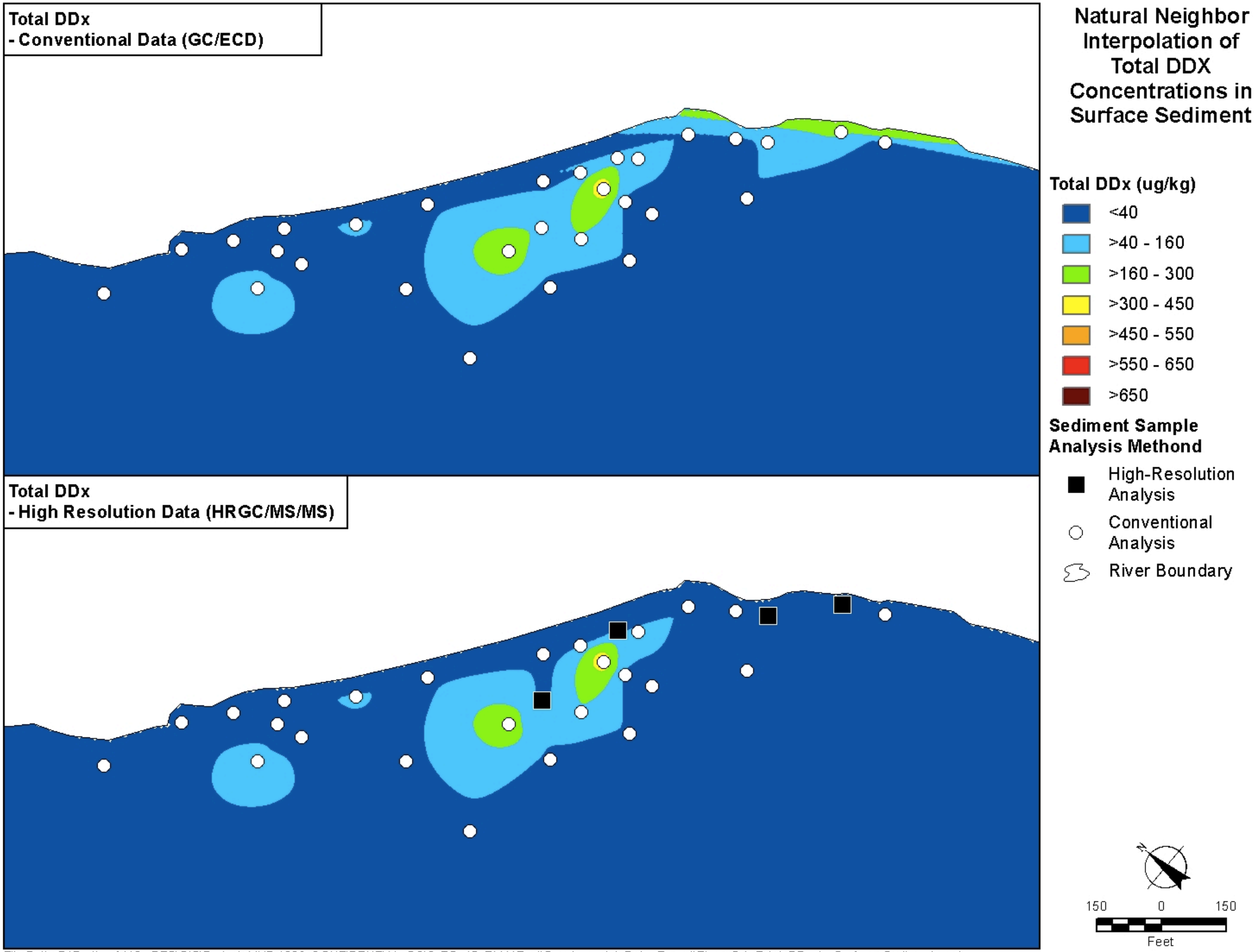
Potential Impact on Data Usability

The reliability of the decisions made are only as good as the quality of the data that is used!

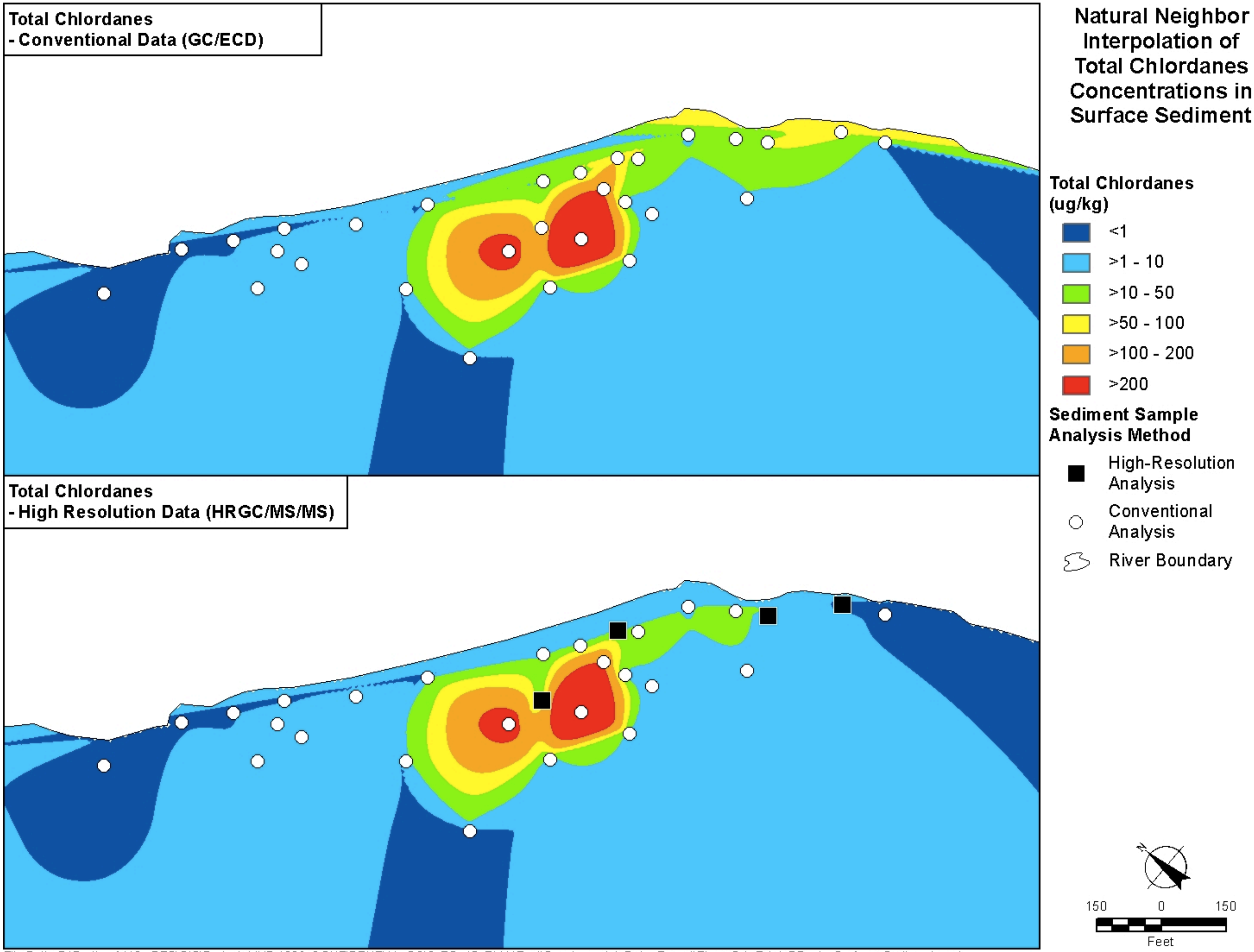
Even if all DQOs and MQOs have been met, the data may not be suitable for their intended purpose(s)

A few thoughts:

- Data are used (in part):
  - Delineating nature and extent of contamination
  - Risk assessment
  - Remedy selection
  - Remedial design
  - Performance monitoring and site closure
  - Cost Allocation and litigation
- Bottom line is may expend unnecessary time and money!


Total DDx
- Conventional Data (GC/ECD)
Total DDx
- High Resolution Data (HRGC/MS/MS)
Natural Neighbor Interpolation of Total DDX Concentrations in Surface Sediment
Total DDx (ug/kg)
<40
>40 - 160
>160 - 300
>300 - 450
>450 - 550
>550 - 650
>650
Sediment Sample Analysis Methond
High-Resolution Analysis
Conventional Analysis
River Boundary
150
0
150
Feet

Natural Neighbor Interpolation of Total Chlordanes Concentrations in Surface Sediment



How Can We Do Better?

When all else fails read the directions. Wait, are there any?

Despite what Sherlock Holmes may have said, sometimes it's just not so elementary!

How Can We Do Better?

- Tiered approach using GC/ECD and HRGC/MS/MS more times than not
- Work with regulatory agencies for more use of HRGC/MS/MS as alternative
- Better understanding of uncertainty
- Clearer communication

How can we do better, cont.

- More collaborative research:
  - Regulatory agencies
  - USEPA Regional Laboratories
  - Private sector laboratories
  - Research organizations
  - Academia
  - Private QA/Consulting firms
- Work with instrument manufactures

How can we do better, cont.

- Document findings in peer reviewed journals

  Surprisingly few papers comparing the results of GC/ECD vs. HRGC/MS/MS in contaminated sediments

- What else?
- Any thoughts?

Finally, land ho!
The journey is almost over!

No, not yet…this story will be ongoing

Concluding Remarks

- GC/ECD not always best choice
- Complex matrices are always difficult
- HRGC/MS/MS "relatively" inexpensive and a great alternative
- Degree of bias in a larger data set could be significant
- Effect on interpretation and usability of data

Concluding Remarks, *(cont.)*:

- Similar bias shown in biotic samples:
  - Battelle Duxbury (2001); biological tissue trends in Boston Harbor lobster
  - Integral Consulting, Inc. (2005); Aroclor interference of chlorinated pesticides in tissue samples by GC/MS-Ion Trap
- This bias is not a new issue, in either abiotic or biotic samples!

Concluding Remarks, *(cont.)*:

- Instrument manufacture examples:
  - Agilent Technologies (e.g., Analysis of Complex Samples by GC/MS/MS – Pesticides in Marine Biota)
  - Thermo Scientific (e.g., Application Note- 10017, Comparison of GC/MS/MS to GC/MS Analysis of Pesticides in Vegetables)
  - Waters Corporation (e.g., Application Note: The Advantages of Using GC/MS/MS for the Analysis of Trace Components in Complex Matrices)

Concluding Remarks, *(cont.)*:

- The data must support the decisions made
- Identify the overall quality (and the limitations) of the data
- Establish how much uncertainty is acceptable
- Always make sure the data are:
  - Scientifically meaningful
  - Valid and usable for their intended purpose
- Remember, we can always do better!

Acronyms

- COIs – Chemicals of Interest
- DQA – Data Quality Assessment
- DQO – Data Quality Objective
- GC/ECD- Gas Chromatography/Electron Capture Detection
- HRGC/MS/MS – High Resolution Gas Chromatography/Mass Spectrometry/Mass Spectrometry
- MQO – Measurement Quality Objective
- PCB – Polychlorinated Biphenyl
- PCDD – Polychlorinated dibenzo-*p*-dioxin
- PCDF – Polychlorinated dibenzofuran
- PAHs – Polycyclic Aromatic Hydrocarbons
- PHC – Petroleum Hydrocarbon
- PQO – Project Quality Objective
- QA/QC – Quality Assurance/Quality Control
- RLs – Reporting limits
- SVOC – Semivolatile Organic Compound

References

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Comparison of two analytical methods for measurement of chlorinated pesticides and PCB congeners in biological tissue- Trends in Boston Harbor lobster tissue. October 2001. *Submitted to* Massachusetts Water Resources Authority Environmental Quality Department, Charlestown Navy Yard, Boston, MA. *Prepared by:* Lisa F. Lefkovitz Jerry M. Neff Robert Lizotte Maury Hall, Battelle Duxbury, Duxbury, MA

A Unique Approach for Evaluating Aroclor Interferences of Chlorinated Pesticides in Tissue for Portland Harbor Superfund Site. L. Jones (Integral Consulting, Inc., Portland, OR), M. Tritt (Integral Consulting, Inc., Mercer Island, WA), and J. Grindstaff (Columbia Analytical Services, Inc. Kelso, WA). Poster Presentation SETAC 2005

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U.S. EPA 2010. SW-846 on-line. Test methods for evaluating solid wastes, physical/chemical methods. www.epa.gov/epawaste/hazard/testmethods/sw846/online/index.htm. Last updated on September 4, 2013. U.S. Environmental Protection Agency, Office of Solid Waste, Washington, DC.

- Method 8018B. Organochlorine Pesticides by Gas Chromatography.
- Method 8082B. Polychlorinated Biphenyls (PCBs) by Gas Chromatography

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- You, the audience for your patience and attention
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- The client(s) who need to remain confidential

DISCLAIMER

- The views and opinions expressed in this presentation are those solely of this presenter and do not necessarily reflect the opinions, official policy, or position of GSI Water Solutions, Inc., the clients, and/or any regulatory agency.
- The information presented herein is an example on how different analytical methods may be used to meet DQOs, PQOs, and aid in the decision-making.
- Third parties are not authorized to use any of the information contained within this presentation without the express written authorization from GSI Water Solutions, Inc.

Thank you!

Any Questions?

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