

CHALLENGES AND ADVANCES IN THE ULTRA-TRACE ANALYSIS OF CONTAMINATED SEDIMENTS USING ISOTOPE-DILUTION (ID) SIM HRGC/HRMS

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SGS Analytical Perspectives

AGENDA

- First & Second Principles
- Challenges
- Solutions
- Data Quality Objectives
- Take-Homes

FIRST PRINCIPLE

- Without direction, we quickly get lost
 - The goal of sampling is to capture an accurate representation of an environment's contents
 - The goal of subsampling is to capture an accurate representation of a sample's contents



SECOND PRINCIPLE

■ Ideal Situation:

$$\Delta S = S' - S = 0$$

in which:

ΔS = change in state of sample before spiking

S' = state of sampled when spiked

S = state of sample upon arrival at lab

■ Processes to avoid if possible:

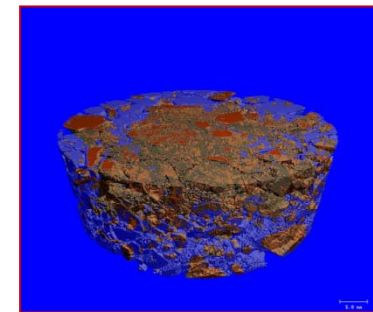
Grinding



Drying

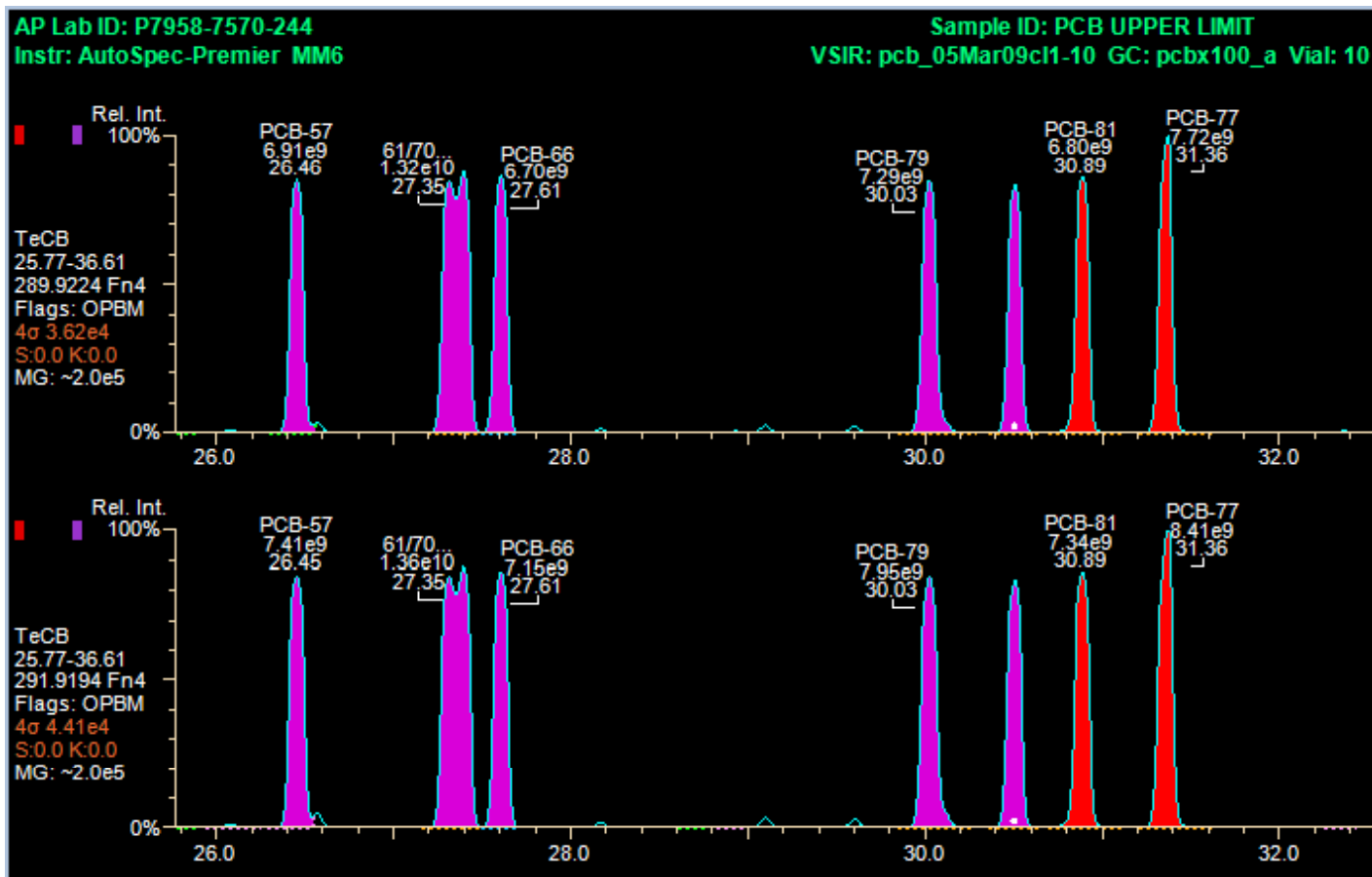


Freeze/Thaw Cycles



DETECTOR SATURATION

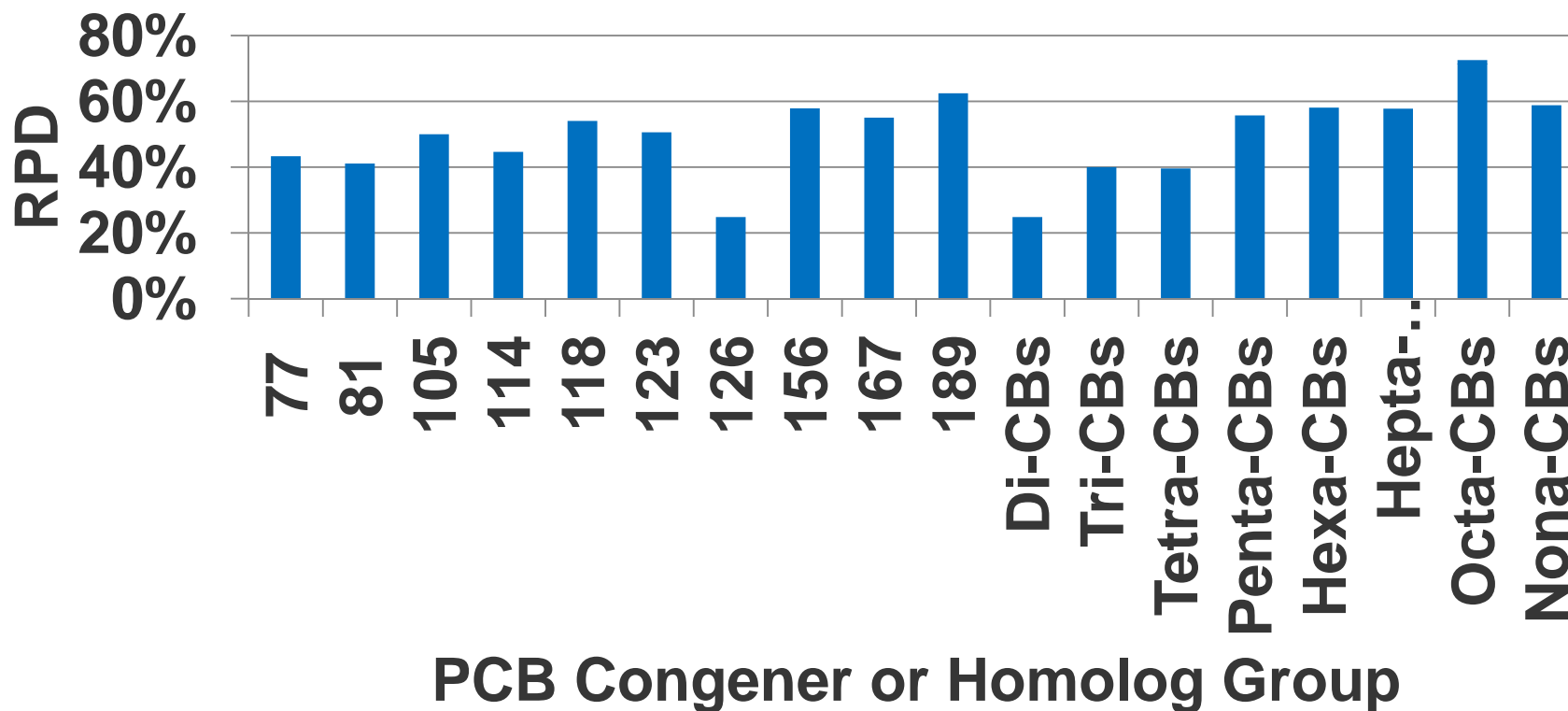
10-g samples can cause detector saturation



UNREPRESENTATIVE SAMPLES

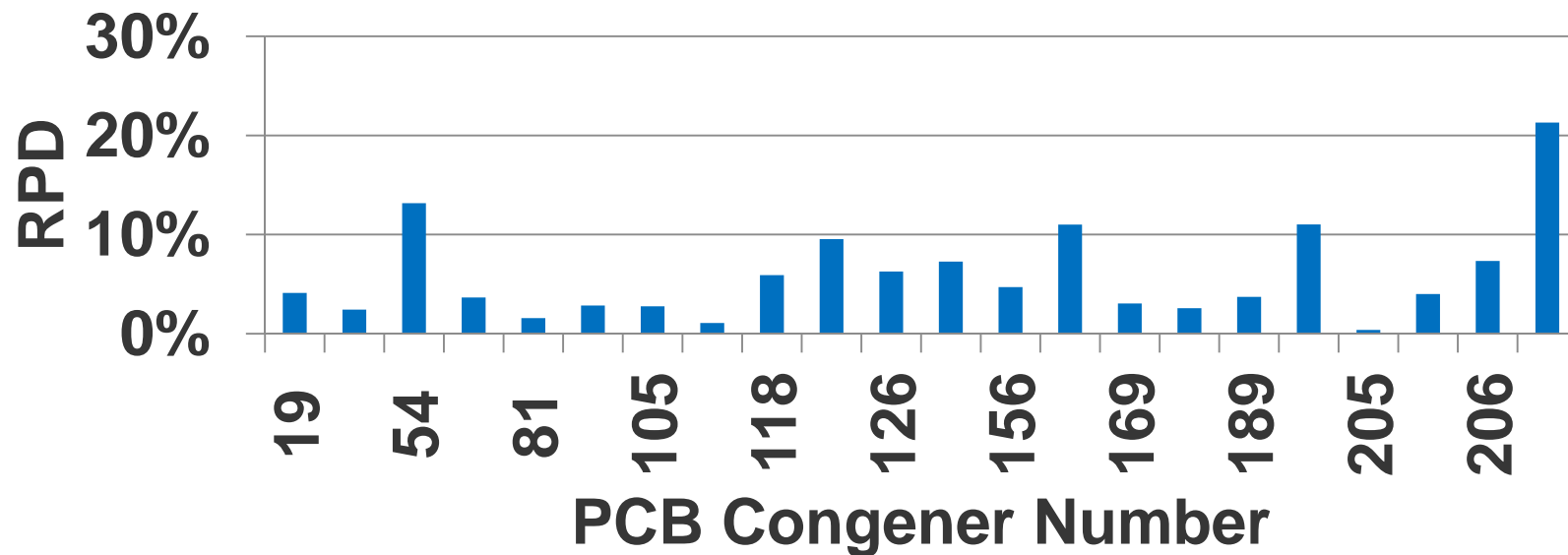
Sample inhomogeneity results in unrepresentative samples

RPDs Produced from "Duplicate" Analysis



USE THE FULL RANGE OF THE MASS SPECTROMETER

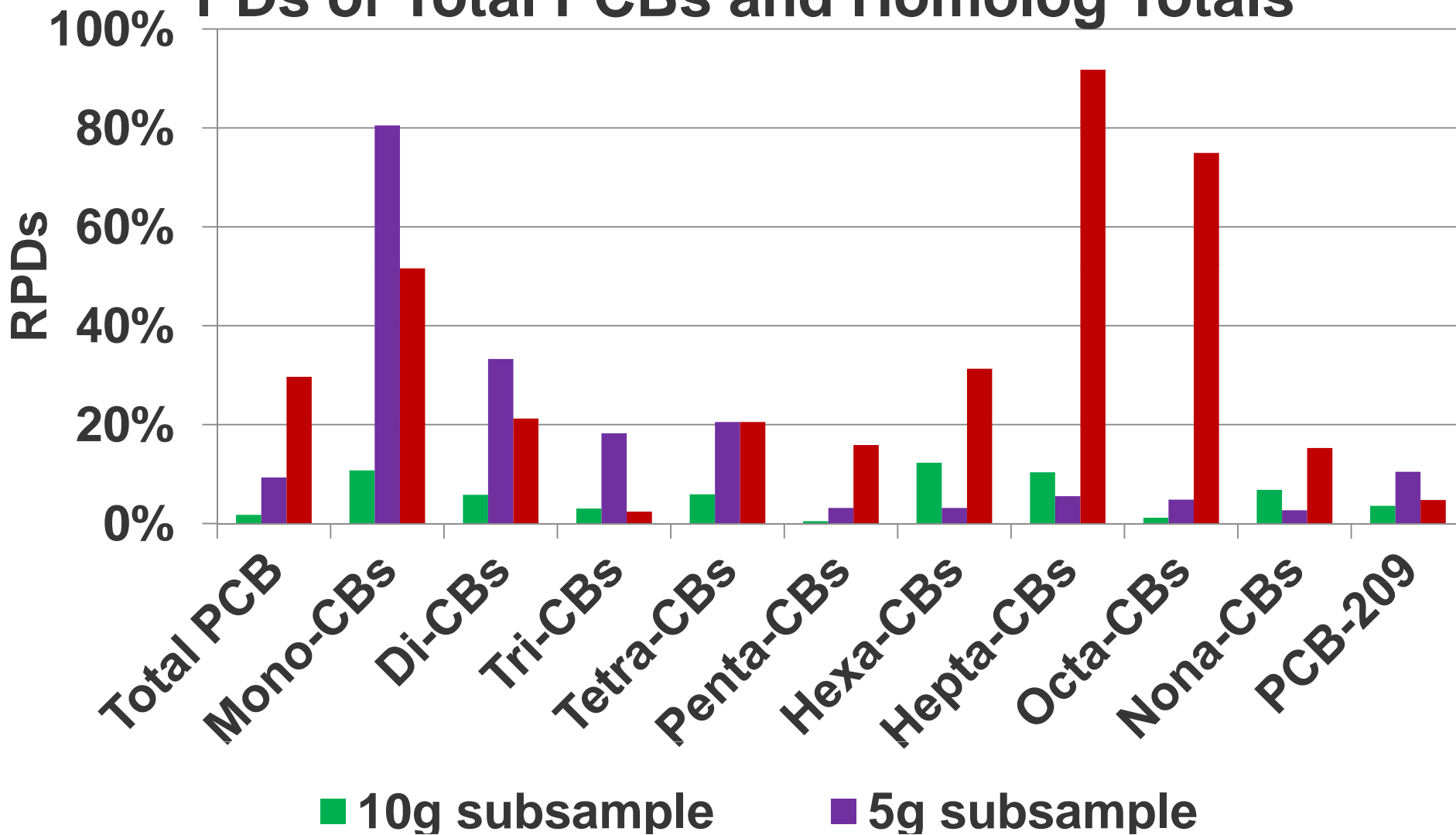
Agreement between Measurements at the Middle of the Calibration Curve and at Concentrations Near Saturation Concentrations



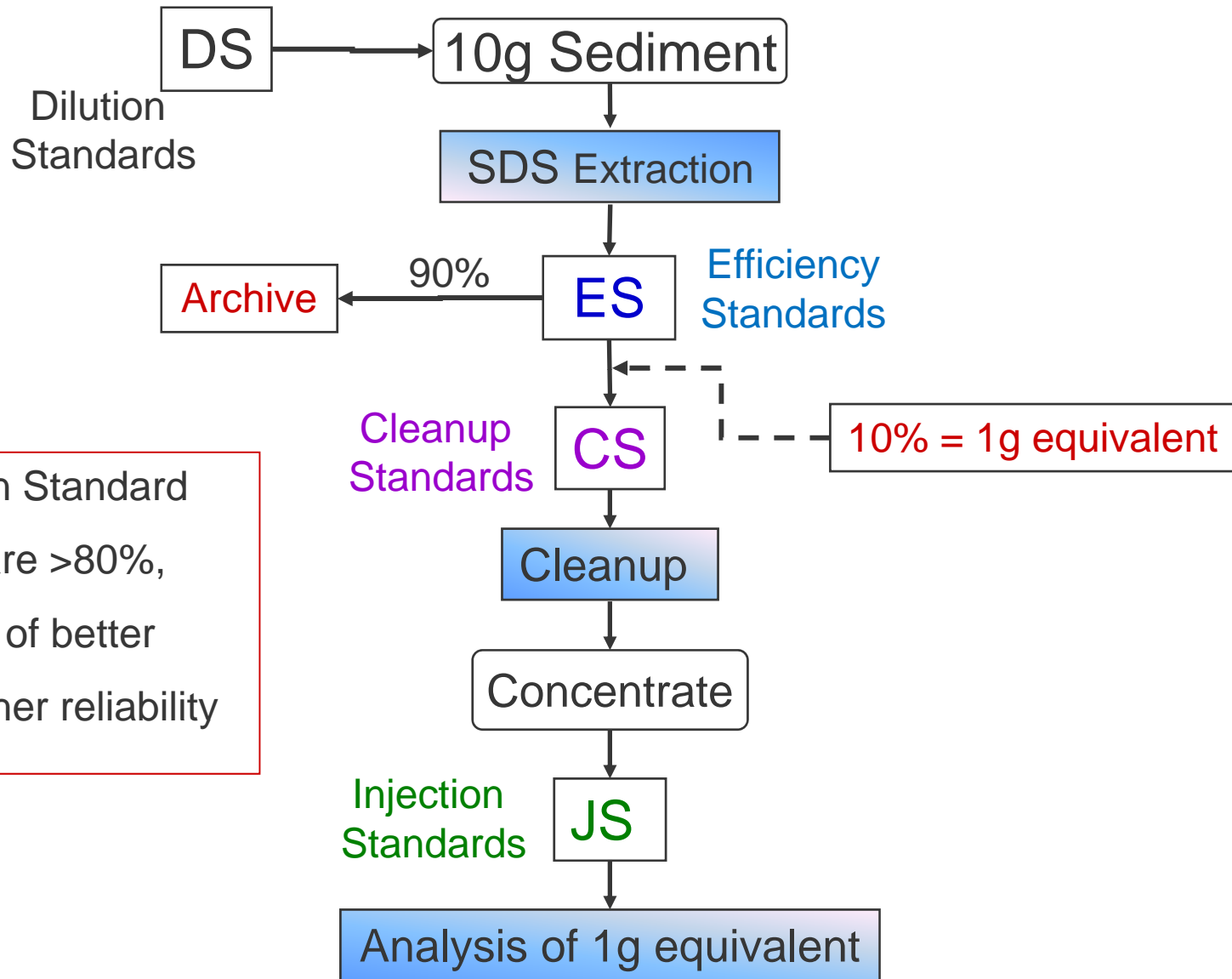
SMALLER SAMPLE SIZE?

Smaller samples will reduce saturation, sometimes at a price

PDs of Total PCBs and Homolog Totals



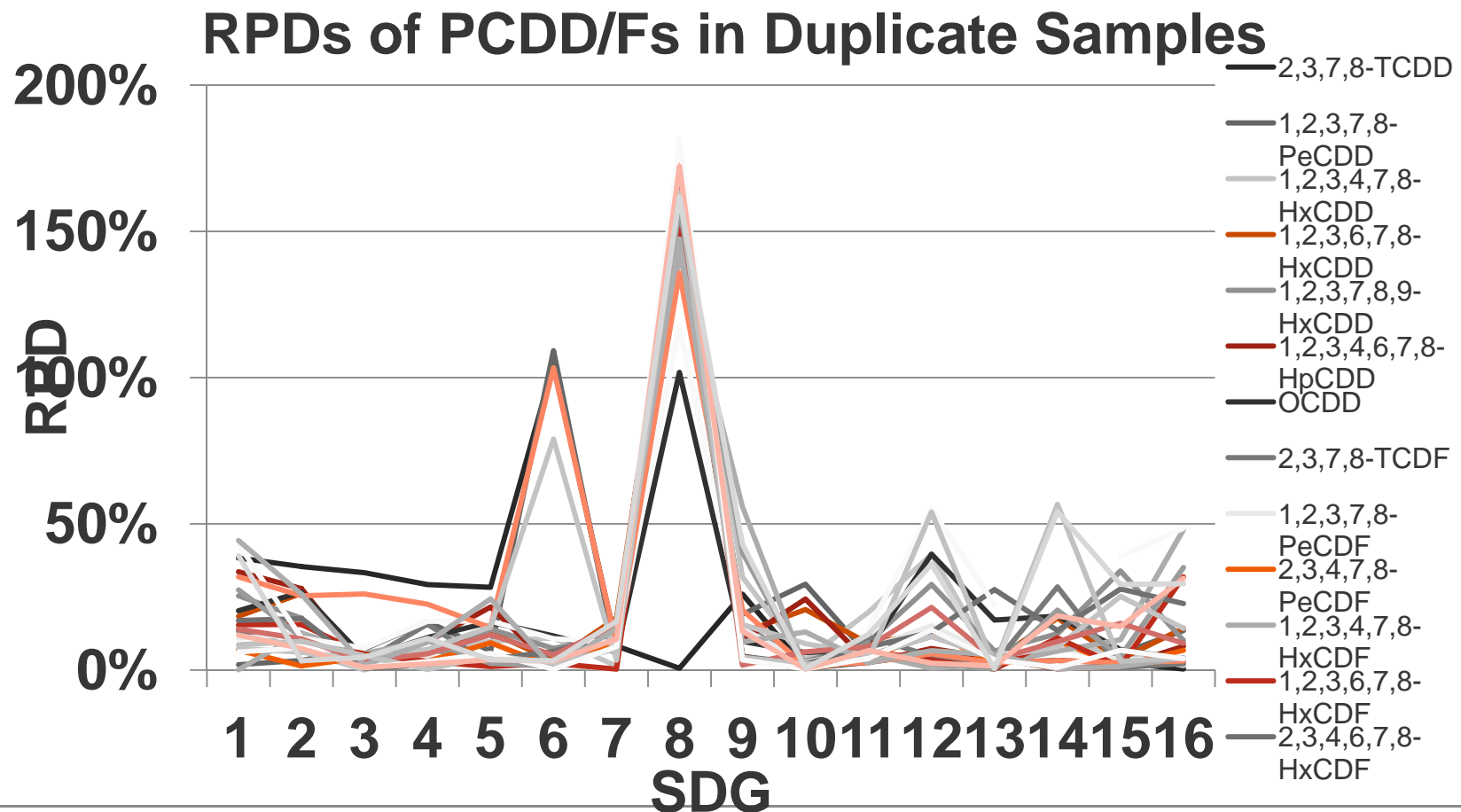
A BETTER OPTION?



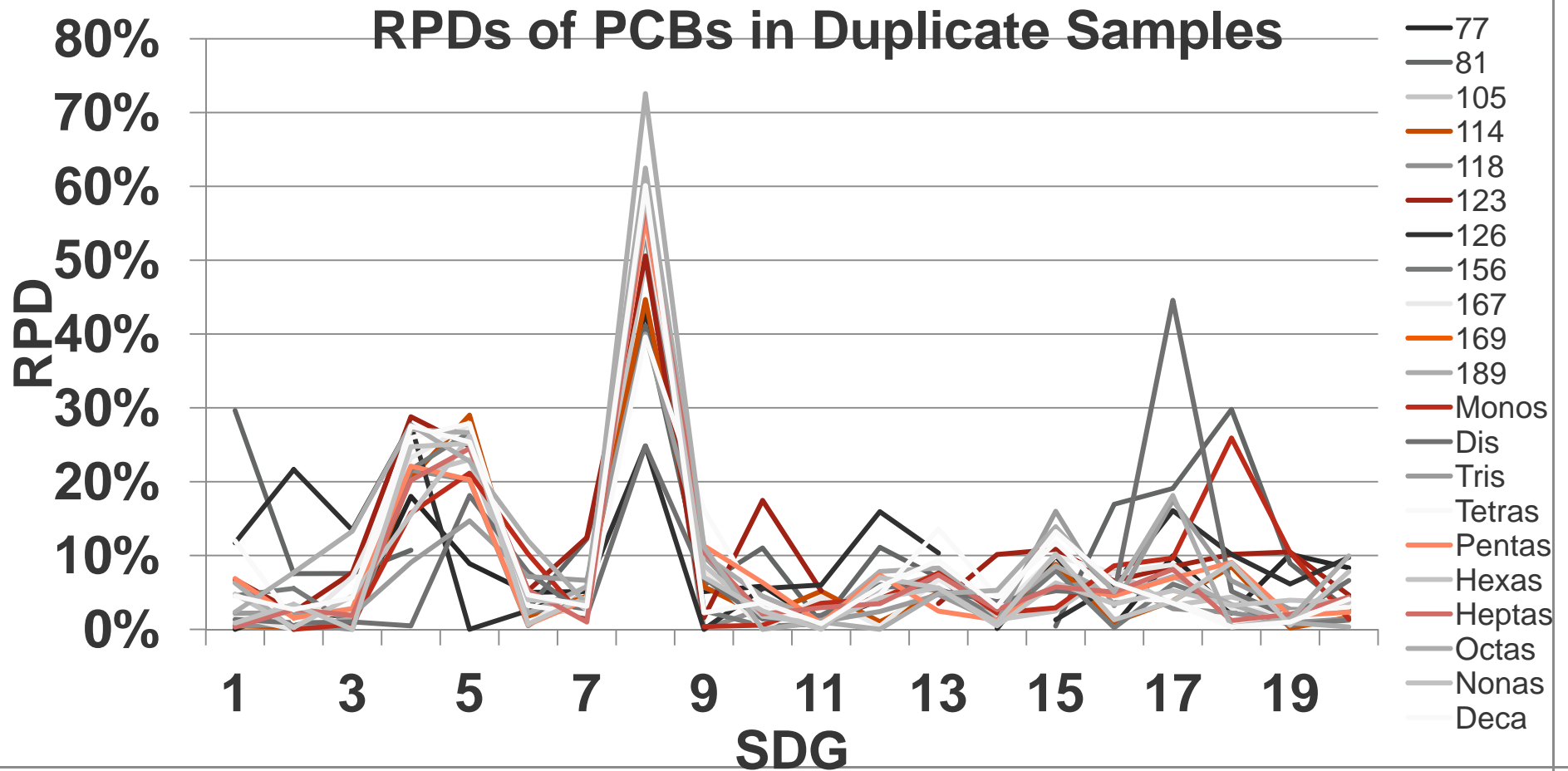
When Dilution Standard recoveries are >80%, data will be of better quality and higher reliability

IS 10G ENOUGH?

These replicates were all 10g – RPDs mostly <20%, but not always



IS 10G ENOUGH?

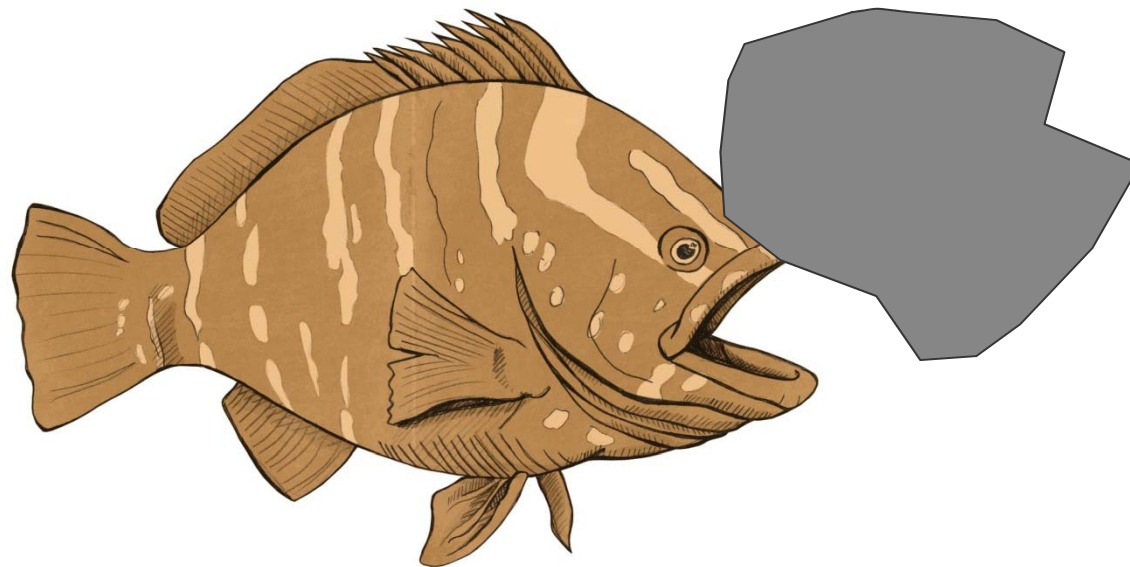


SAMPLE HETEROGENEITY

- These difficulties seem to stem from sample heterogeneity – the question is what to do about it.
- EPA guidance, based on Gy's theory, is only applicable to completely dry samples containing only particulates. It also calls for grinding in many cases.
- Some scientists advocate using Gy theory after modifying the sample to be 100% particulate.
- The fundamental problem with sample modification is that **the lab is no longer analyzing what was submitted!!!**
- The correct solution, then, is to ensure that the sample sent to the lab is the right sample.

DATA QUALITY OBJECTIVES

DQOs should reflect program objectives



For example, fish don't eat boulders – and pebbles aren't relevant to wildlife exposure

CONCLUSIONS

- Contaminated sediments pose challenges for ultra-trace analysis, especially pollutant concentrations and sample inhomogeneity
- Labs should be allowed to use the full range of the mass spectrometer
- Regulators, samplers, and labs should collaborate to develop suitable solutions to this challenge without compromising the science
- **Sample modification should be avoided at all costs!!!**
- These challenges should be considered and addressed by formulating meaningful DQOs during the planning phase (i.e., in QAPPs).

THANK YOU FOR YOUR
ATTENTION – QUESTIONS?