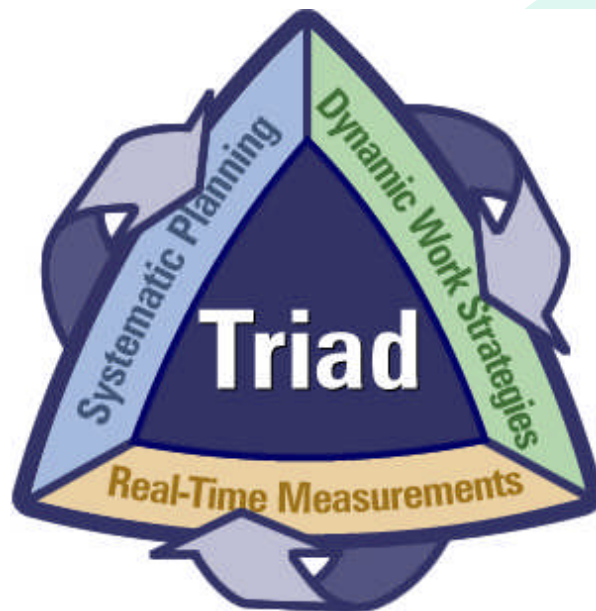


Should XRF Data Be Adjusted Against ICP Data?



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2009 NEMC Conference

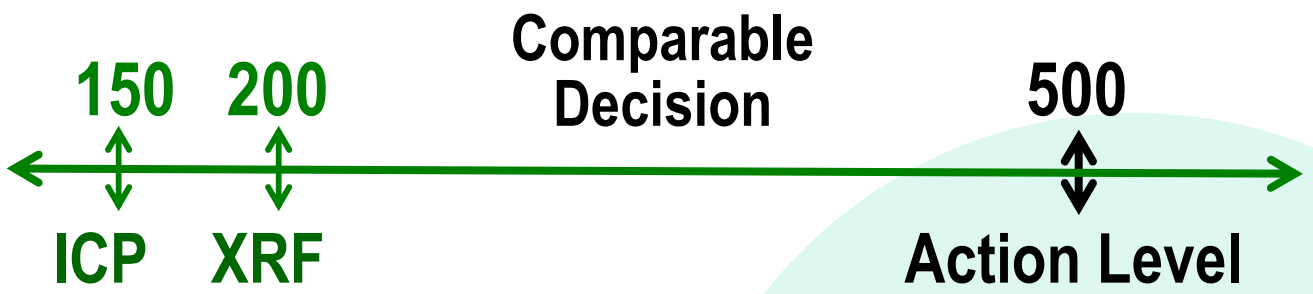
Comparability: What is it?

- Common perception:
 - Run same samples by 2 methods
 - How close are the 2 data sets?
 - Apply fixed limits (<20% RPD, $R^2 \geq 0.9$, etc.)
- Problem: comparability for data on real soil samples is muddled by heterogeneity...no TRUE splits
- More productive perspective:
 - Are 2 sets of data comparable for the purpose of making project decisions?

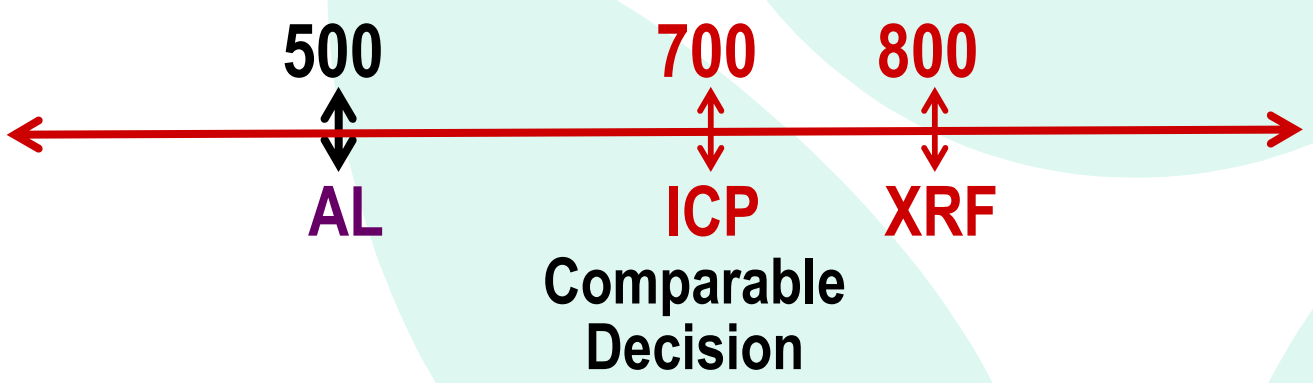
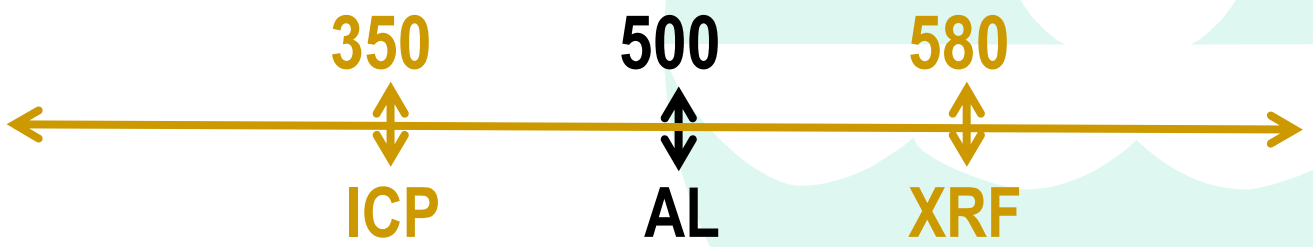
In other words:

 - Do the 2 data sets point to the same answer to the question/decision?

Comparability as “Do the Data Agree wrt Decisions?”



Non-comparable Decision = Decision Uncertainty



Arbitrary Numerical Standards for Comparability

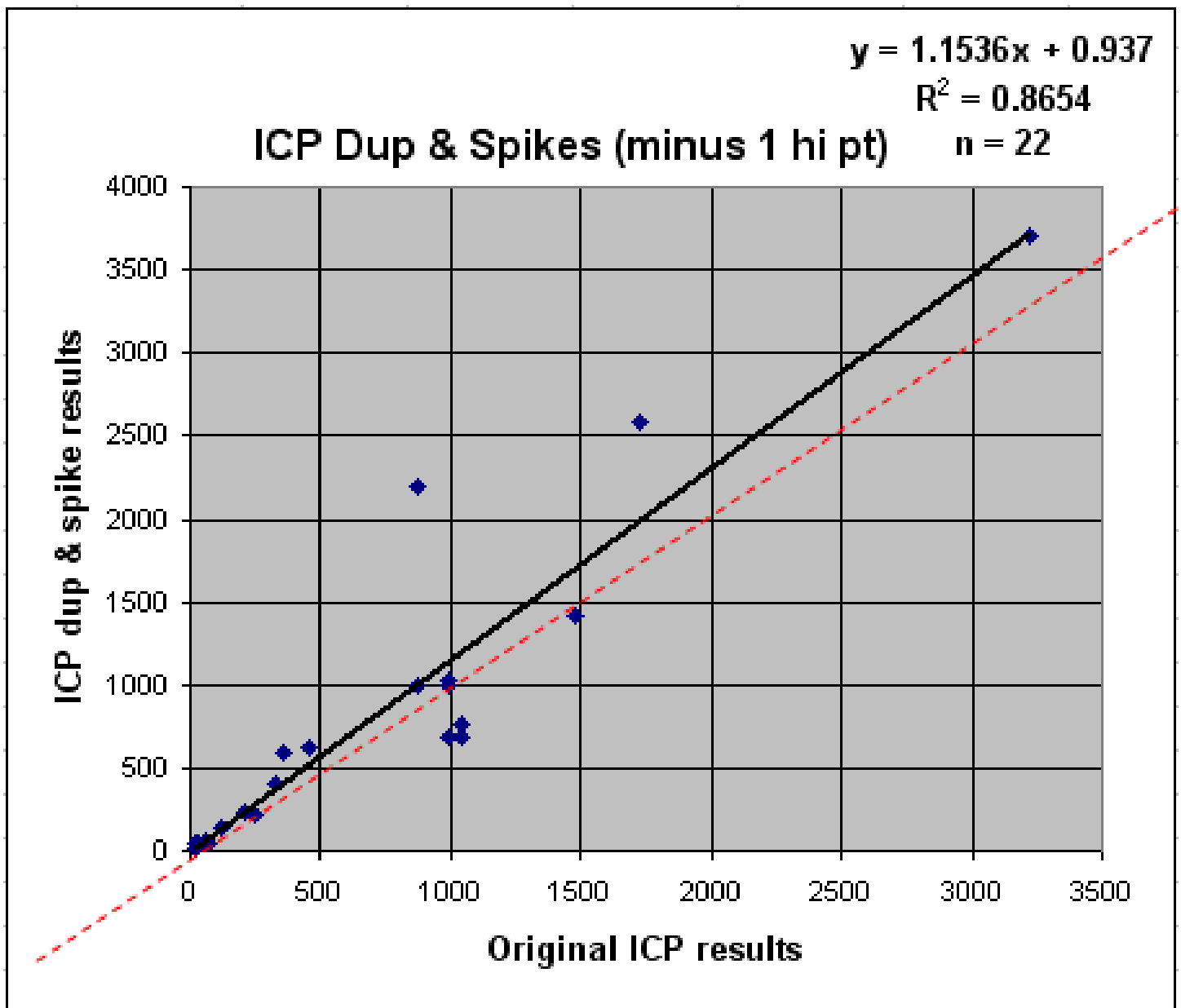
- Example: Lab duplicates for soil within 20% (or 25%, or 30%...) RPD
 - Limits often exceeded because of matrix
 - Data are “J” flagged, but then the J is ignored or removed by data user
- Even when numerical differences seems negligible, math causes division by a low number to give a high RPD
 - 4 ppm & 5 ppm Pb: $RPD = 22.2\%$
 - 400 ppm & 500 ppm Pb: $RPD = 22.2\%$
 - Difference between 400 & 500 ppm much more significant than between 4 & 5 ppm

Duplicates as a Measure of Method Comparability

RCRA XRF project, with data submitted to EPA for review.

- Types of duplicates performed:
 - XRF duplicates (reanalyze a bag),
 - bag splits between XRF and ICP
 - field dups for ICP (replicate bag splits)
 - lab dups for ICP
 - 4 of 18 (22%) of exceeded lab's 35% limit (40.5, 38.1, 49 & 85.8%)
 - “super-duplicates”: 1 bagged soil sample split between XRF & ICP with each method having a lab duplicate

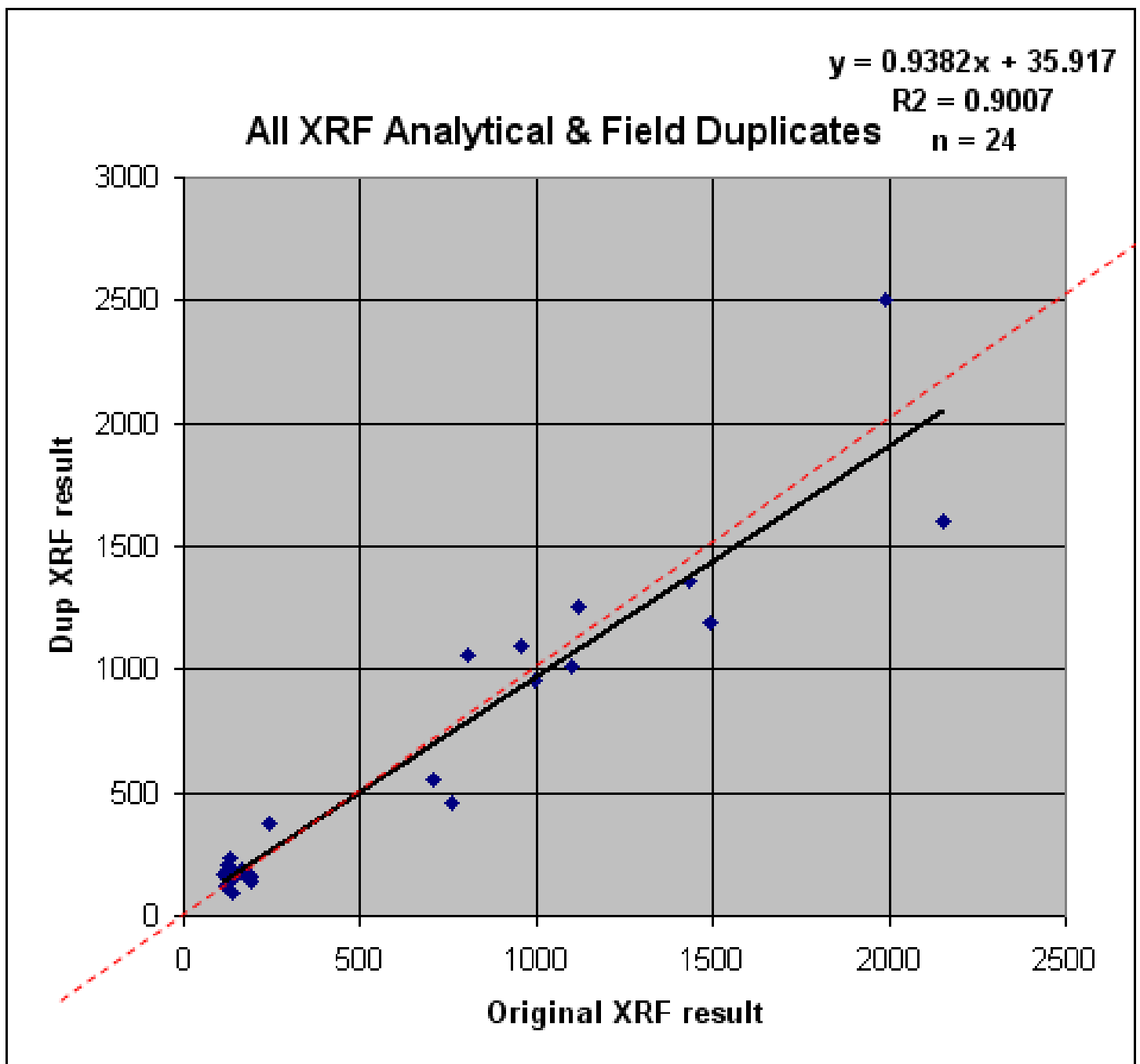
ICP Lab Duplicates: How Much Variability?



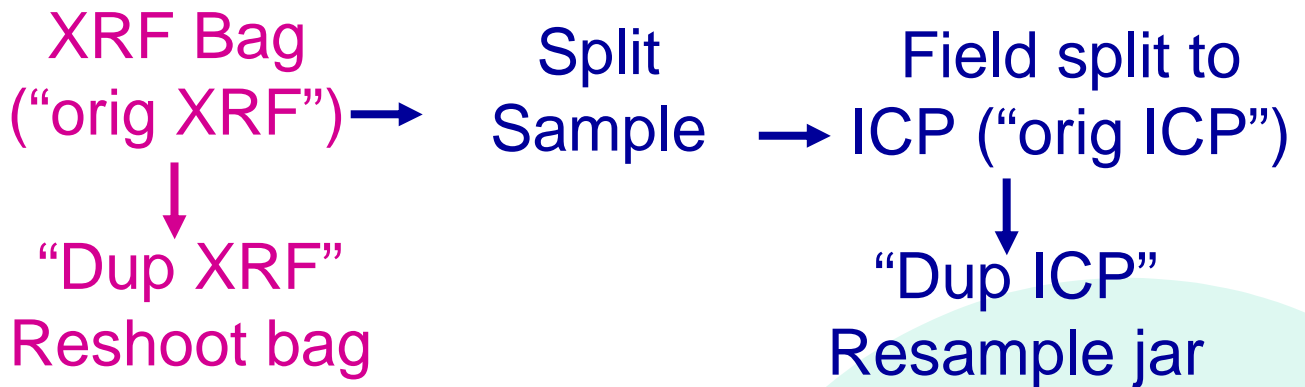
Problem is most certainly sample heterogeneity

XRF Duplicates

Compared to ICP dups:
XRF dups had better slope (0.94 vs 1.15); better R^2 (0.901 vs 0.865), but worse intercept (36 vs 0.9)



“Super-Duplicates”



Analyzing the same samples, evaluate 3 questions:

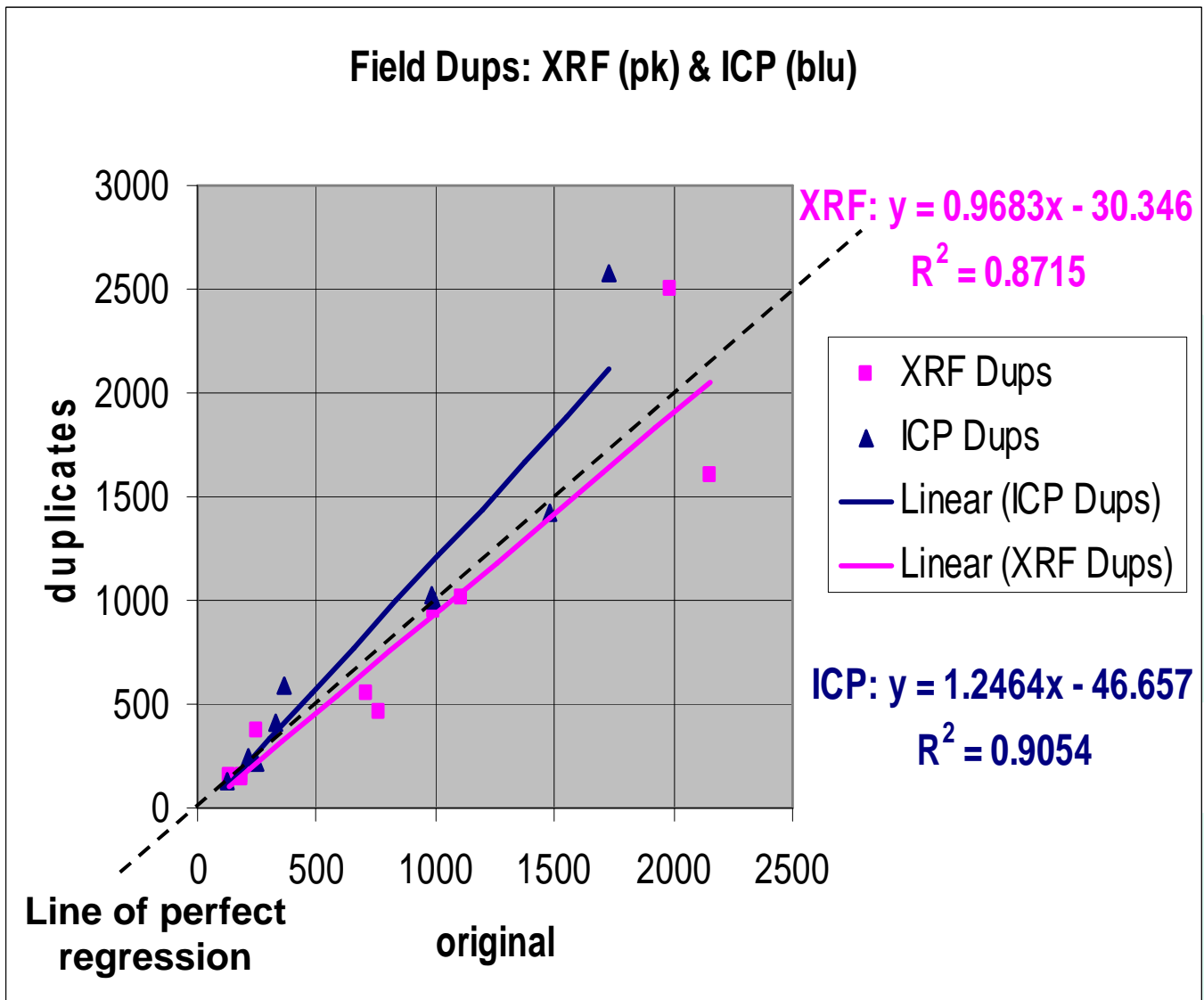
How well does XRF match itself?
(Regression on “Orig XRF” vs “Dup XRF”)

How well does ICP match itself?
(Regression on “Orig ICP” vs “Dup ICP”)

Is the XRF & ICP data sets comparable to each other?

Plot on same graph for easy comparison

XRF dup set is pink
ICP dup set is blue



Compare Regressions

XRF vs. XRF has poorer R^2 , but better slope & intercept

ICP vs. ICP has slightly better R^2 , but worse slope & intercept (deviates farthest from ideal regression line)

3rd Question

Are the 2 lines “different”?

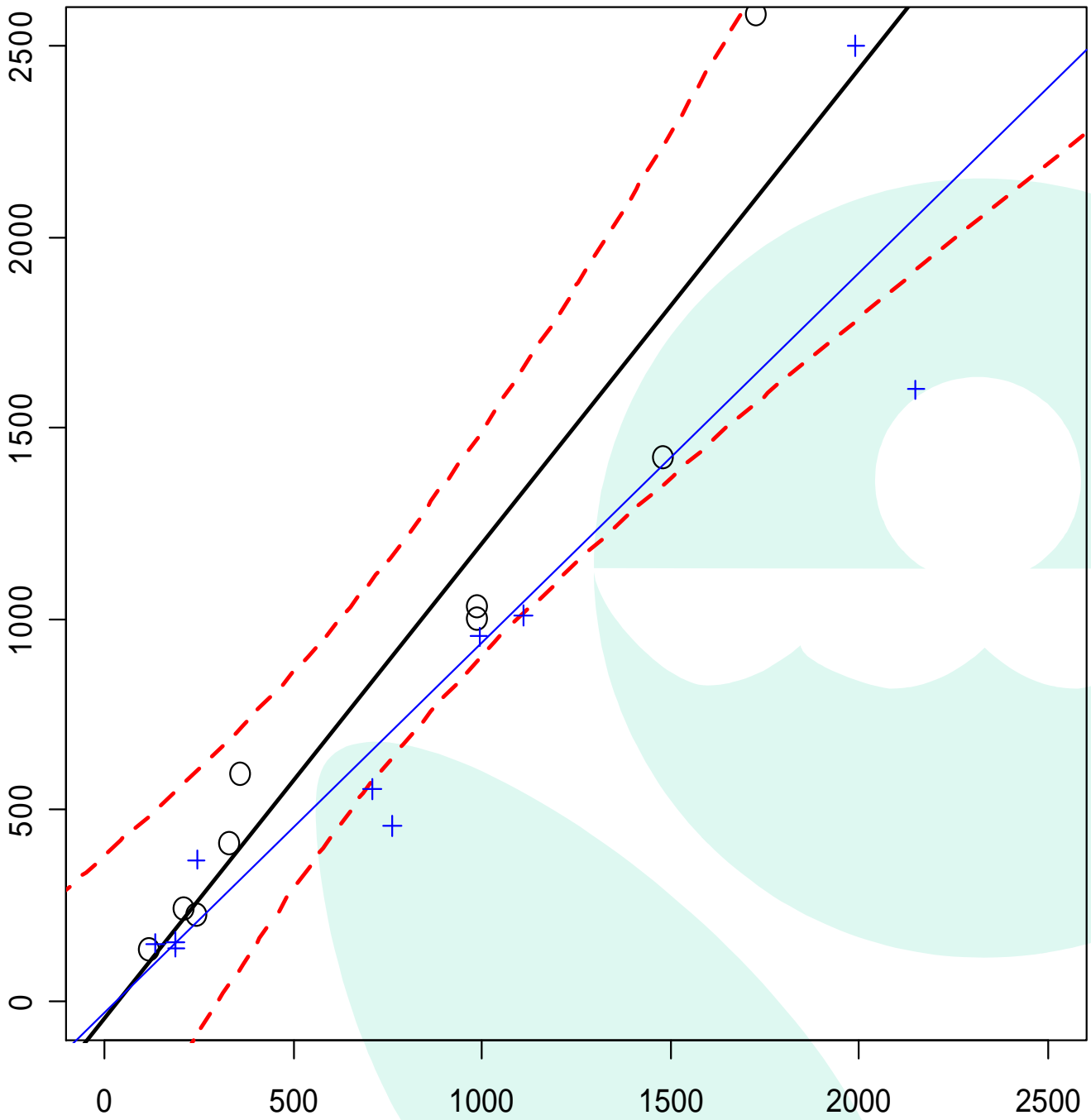
In other words, are the XRF results statistically different from the ICP's so that the XRF results should be adjusted to improve comparability to ICP?

Evaluating 2 regression lines for statistical equivalence

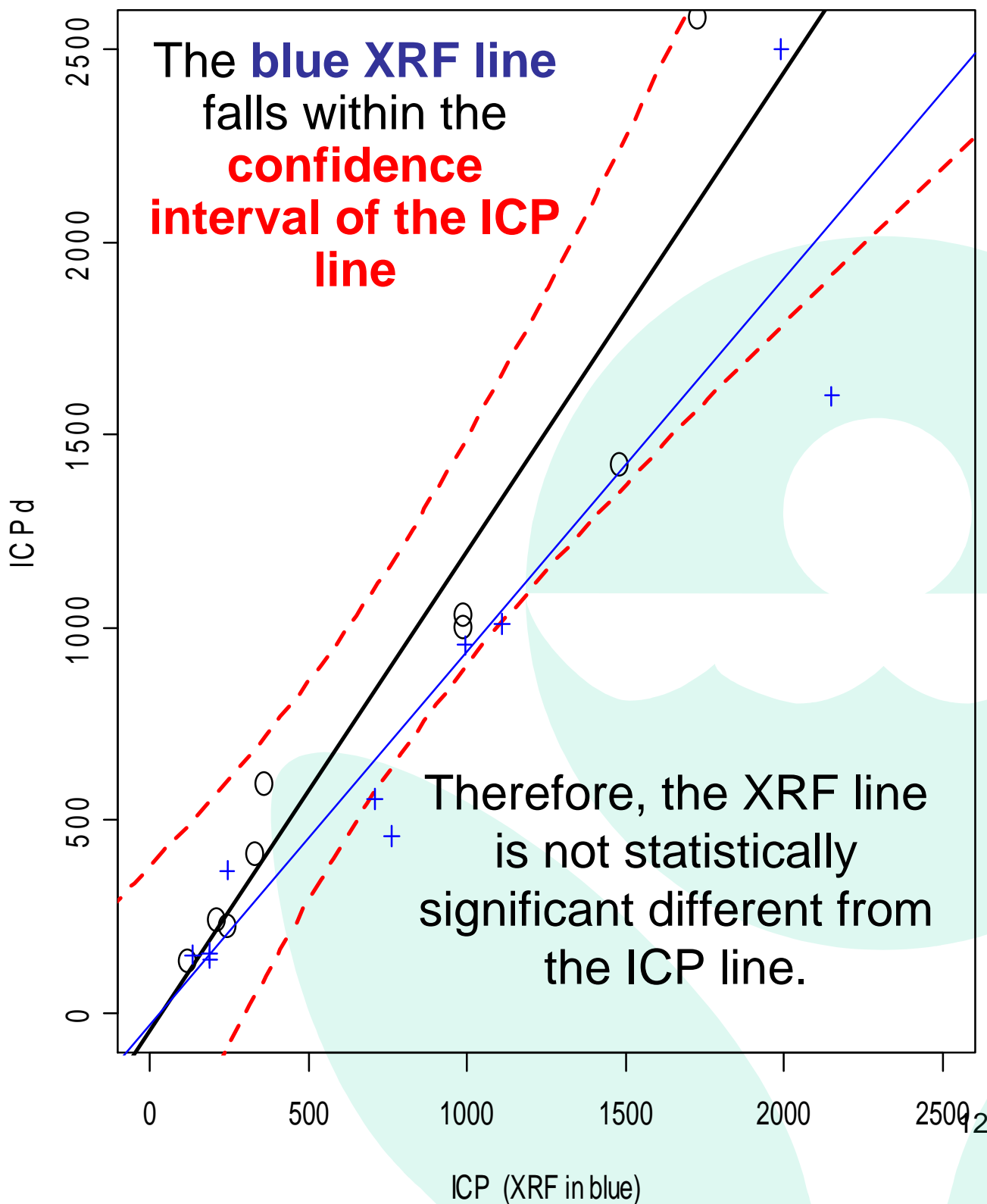
Use statistical software to draw confidence limits (CLs) around the regression lines.

See if regression line of one falls within the confidence interval of the other.

Draw the 95% **confidence interval** around **one of the regression lines** & see if **the other line** falls within it.



ICP data are circles. Their regression line is black. The confidence interval is within the **red lines**. The **blue X's** are the XRF data, and the **blue line** is the XRF regression.



When XRF data are compared to ICP data, the common assumption is that ICP is the right answer, and XRF data must match ICP data to be “good”.

But a fair question is:
How well is the ICP data
matching itself in a regression?

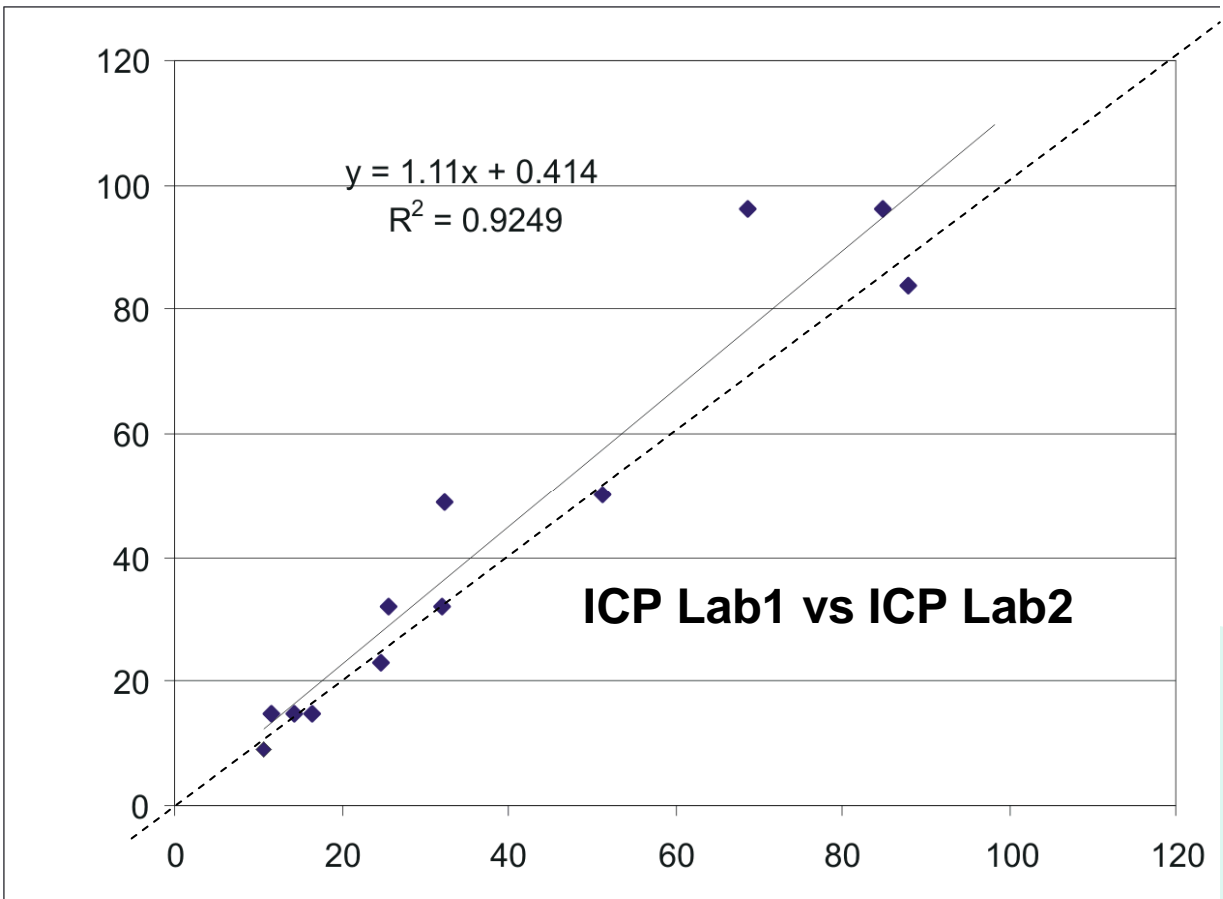
Because...
XRF data cannot match the ICP data
any better than the ICP data can
match itself.

Comparability for Soil Samples is Hostage to Sample Prep

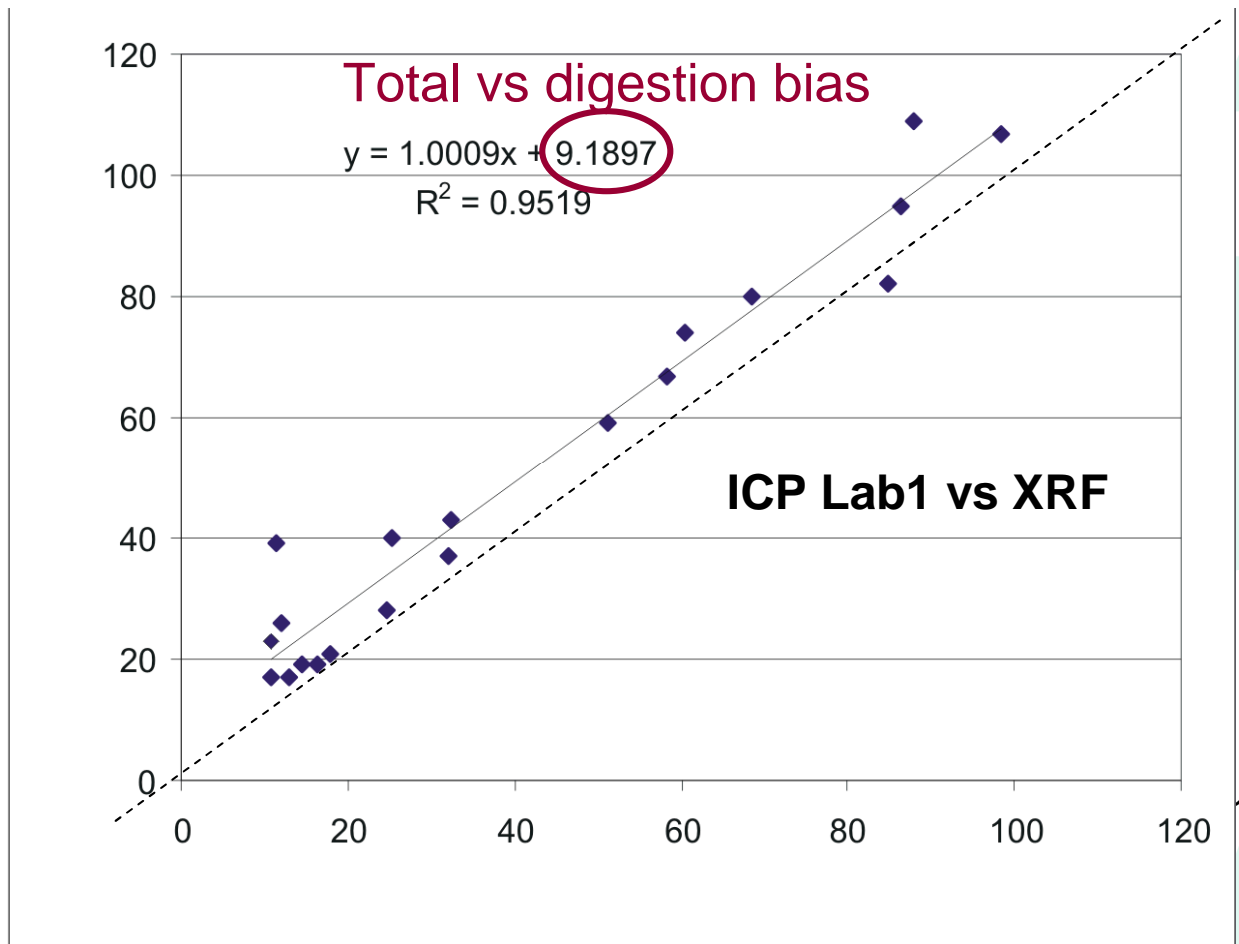
Most of the “matching” between

- ICP & its duplicates, and
- XRF & its duplicates, and
- XRF vs ICP

is directly attributable to the
thoroughness of sample
homogenization



Real project...well homogenized samples...As data



If there is no statistical difference between an XRF-ICP regression and an ICP-ICP regression, then adjustment (“correction”) of the XRF data set is not warranted.

Adjusting it would make as much sense as adjusting ICP Lab1 data to better match ICP Lab2 data.

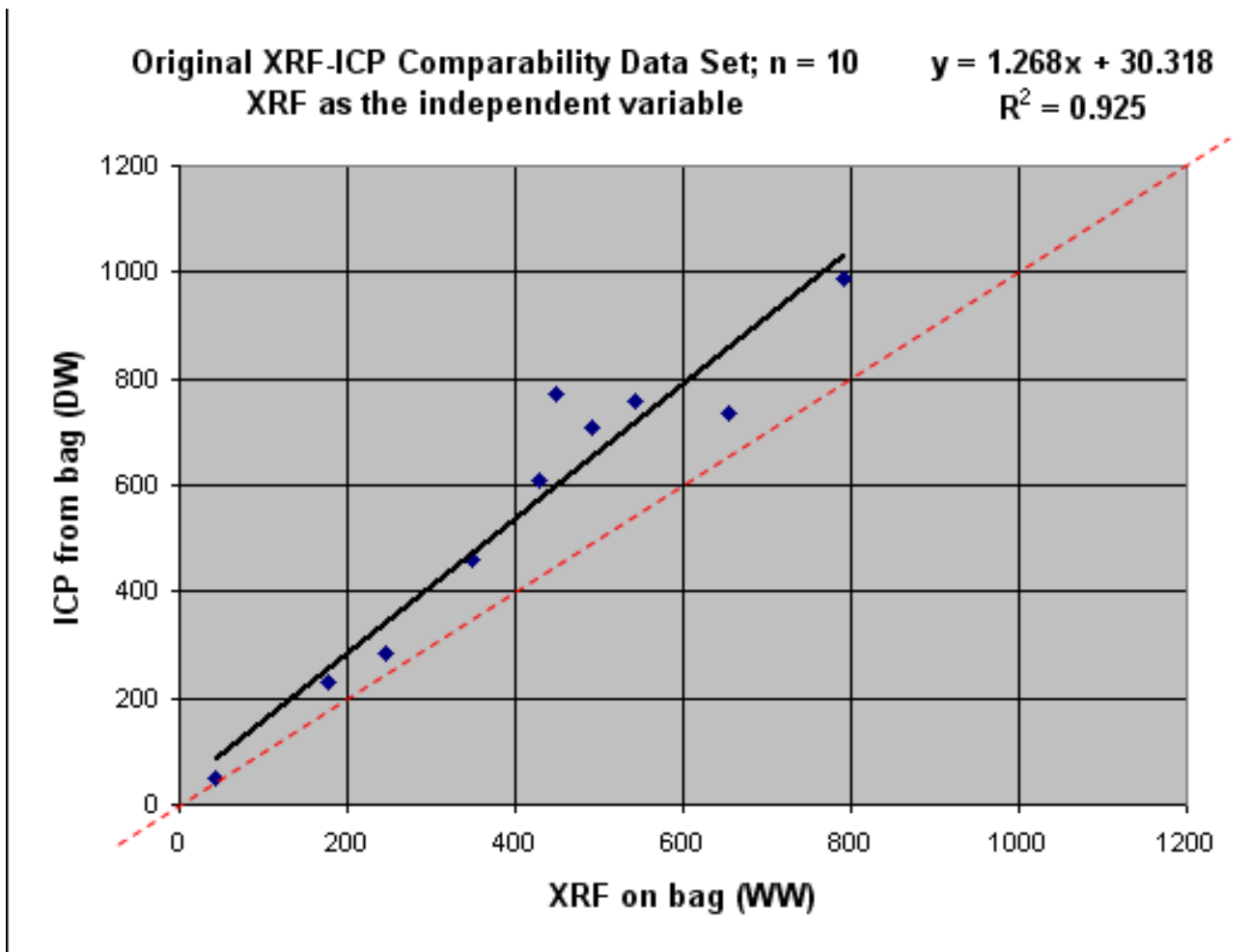
Sometimes XRF & ICP data are not comparable

Can be a clue that something is wrong & needs to be investigated

A Project Example

- ❖ XRF done on bags, paired ICP samples taken from bag
- ❖ Statistical evaluation showed the XRF & ICP data were statistically different.
- ❖ XRF was significantly biased **LOW** compared to ICP (*unusual*)

Regression of XRF-ICP “splits” had high slope



Fairly good sample homogenization was done

Note: XRF is the independent variable because the goal is to use the XRF-ICP relationship to predict an equivalent result in terms of ICP.

Could it be a Moisture Problem?

- ICP analysis done on wet sample, but is adjusted to DW.
- Check: Select 2 soil bags—1 w/ highest moisture (24%) & 1 with lowest (9%).
- From each bag, dry soil & fill 3 XRF cups.

Sample Moisture	ICP Pb, DW (single result)	Original XRF (bagged, wet) (4-shot ave over bag)	XRF (dried soil, 3 replicate cups)
9%	736	655	802, 802, 771 (ave = 792)
24%	770	474 (4-shot ave over bag)	751, 743, 745 (ave = 746)

- XRF readings much higher on dried samples. Effect at 9% greater than expected. Is something else going on?

Check for Plastic Bag Interference: How?

- Use NIST SRMs
- Replicate XRF readings with & without plastic bag laid over cup
- Is there a reduction in Pb conc. with the plastic? By how much?

SRM Pb conc (ppm)	Ave w/o plastic	Ave w/ plastic	% reduction
432	398	386	3%
1162	1127	1002	11%
5532	5509	4672	15%

- Plastic bag interference causes bias
- Magnitude of interference depends on Pb concentration of sample
- Can an interaction be magnifying moisture effect?

Develop correction equations to address the 2 interferences using a spreadsheet

	A	B	C	D
1		Plastic Bag Correction		
2	XRF (WW)	% reduction by plastic	PB corr XRF = XRF(WW-PB)	
3	448	3.55	464	
4		= 0.0111*(A2) -1.4222	= A2/(1-(B2/100))	
5				
6	Take PlasticBag-corrected value and correct it for DW			
7				
8	XRF (WW-PB)	% solids data	% moisture	XRF as PB-DW
9	464	82	18	566
10				= A9/B9*100

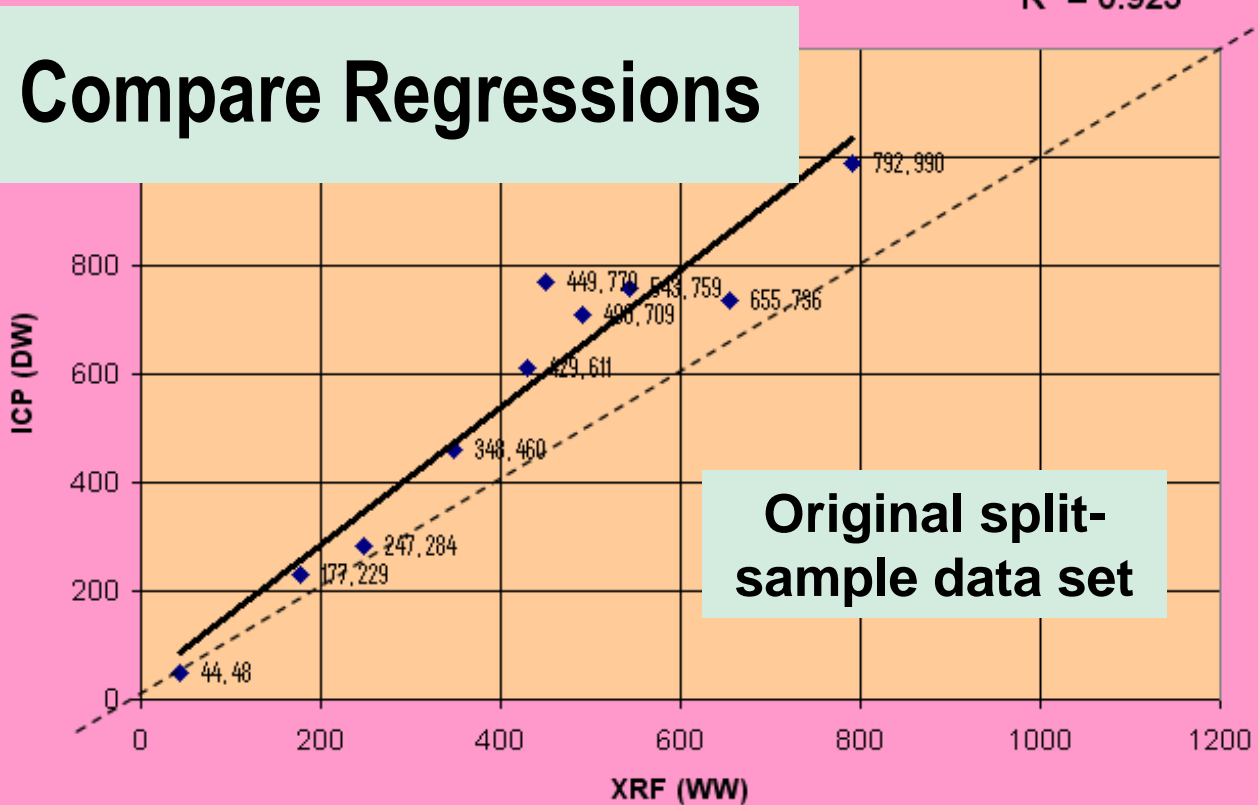
- ❖ Apply corrections sequentially
- ❖ Evaluate effect of corrections by comparing (by regression) each against ICP results

Simple XRF vs ICP Regression

$$y = 1.268x + 30.318$$

$$R^2 = 0.925$$

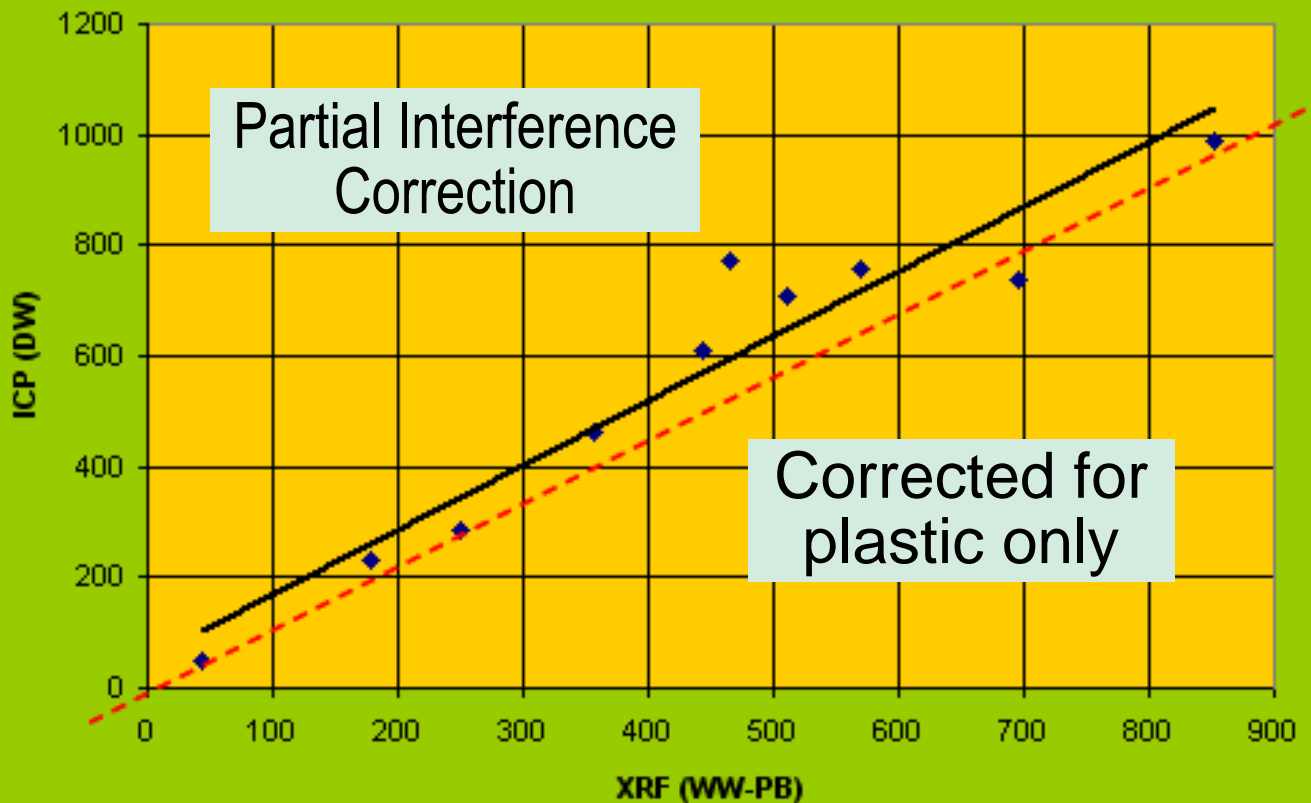
Compare Regressions



Eval Plastic Correction using Linear Correction Eqn

$$y = 1.167x + 50.165$$

$$R^2 = 0.917$$



Comparing the Regressions

Regression between...	Slope	y-intercept	R ²
Original XRF vs ICP	1.27	30	0.925
XRF (corrected for plastic) vs ICP	1.17	50	0.917
XRF (corrected for moisture) vs ICP	1.13	1.1	0.973
XRF (corrected for both) vs ICP	1.04	21	0.966

- ❖ The corrected XRF data produced different decisions than would have been made using the uncorrected data.
- ❖ But the corrected data were comparable to the ICP data wrt decisions.

QUESTIONS?

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