Summer 7-5-2023

# Butte Priority Soils Operable Unit (BPSOU) Field XRF to Laboratory Correlation and Regression Analysis Procedure for Unreclaimed (UR) and Insufficiently Reclaimed (IR) Sites

Mike McAnulty

Pioneer Technical Services, Inc.

**Atlantic Richfield Company**

**Mike Mc Anulty**
Liability Manager

317 Anaconda Road
Butte MT 59701
Direct (406) 782-9964
Fax (406) 782-9980

July 5, 2023

Nikia Greene
Remedial Project Manager
US EPA – Montana Office
Baucus Federal Building
10 West 15th Street, Suite 3200
Helena, Montana 59626

Erin Agee
Senior Assistant Regional Counsel
US EPA Region 8 Office of Regional Counsel
CERCLA Enforcement Section
1595 Wynkoop Street
Denver, CO 80202
Mail Code: 8ORC-C

Daryl Reed
DEQ Project Officer
P.O. Box 200901
Helena, Montana 59620-0901

Jonathan Morgan, Esq.
DEQ, Legal Counsel
P.O. Box 200901
Helena, Montana 59620-0901

**RE: Butte Priority Soils Operable Unit (BPSOU) Field XRF to Laboratory Correlation and Regression Analysis Procedure for Unreclaimed (UR) and Insufficiently Reclaimed (IR) Sites**

Agency Representatives:

I am writing to you on behalf of Atlantic Richfield Company to submit the Field XRF to Laboratory Correlation and Regression Analysis Procedure for Unreclaimed (UR) and Insufficiently Reclaimed (IR) Sites within the Butte Priority Soils Operable Unit (BPSOU). The referenced technical memo describes the proposed methodology and application of regression analysis.

The document may be downloaded at the following link:

https://pioneertechnicalservices.sharepoint.com/:f:/s/submitted/Etbib_6zfVVHu5u7NJg62YsB_wD2GukChDGGsRMCbAB3qg.

If you have any questions or comments, please call me at (907) 355-3914.

Sincerely,

Mike McAnulty

Mike Mc Anulty
Liability Manager
Remediation Management Services Company
An affiliate of **Atlantic Richfield Company**

**Atlantic Richfield Company**

**Mike Mc Anulty**
Liability Manager

317 Anaconda Road
Butte MT 59701
Direct (406) 782-9964
Fax (406) 782-9980

Cc: Chris Greco / Atlantic Richfield – email
Josh Bryson / Atlantic Richfield – email
Loren Burmeister / Atlantic Richfield – email
Dave Griffis / Atlantic Richfield – email
Jean Martin / Atlantic Richfield – email
Irene Montero / Atlantic Richfield – email
David A. Gratson / Environmental Standards – email
Mave Gasaway / DGS – email
Adam Cohen / DGS – email
Brianne McClafferty / Holland & Hart – email
David Shanight / CDM – email
Curt Coover / CDM – email
James Freeman / DOJ – email
Amy Steinmetz / DEQ – email
Dave Bowers / DEQ – email
Carolina Balliew / DEQ – email
Katie Garcin-Forba / DEQ – email
Jim Ford / NRDP – email
Pat Cunneen / NRDP – email
Katherine Hausrath / NRDP – email
Ted Duaime / MBMG – email
Gary Icopini / MBMG – email
Becky Summerville / MR – email
John DeJong / UP – email
Robert Bylsma / UP – email
John Gilmour / Kelley Drye – email
Leo Berry / BNSF – email
Robert Lowry / BNSF – email
Brooke Kuhl / BNSF – email
Lauren Knickrehm / BNSF – email
Doug Brannan / Kennedy Jenks – email
Matthew Mavrinac / RARUS – email
Harrison Roughton / RARUS – email
Brad Gordon / RARUS – email
Mark Neary / BSB – email
Eric Hassler / BSB – email
Julia Crain / BSB – email
Brandon Warner / BSB – email
Abigail Peltomaa / BSB – email
Eileen Joyce / BSB – email
Sean Peterson/BSB – email
Josh Vincent / WET – email
Scott Bradshaw / W&C – email

**Atlantic Richfield Company**

**Mike Mc Anulty**
Liability Manager

317 Anaconda Road
Butte MT 59701
Direct (406) 782-9964
Fax (406) 782-9980

Emily Stoick / W&C – email
Pat Sampson / Pioneer – email
Andy Dare / Pioneer – email
Karen Helfrich / Pioneer – email
Randa Colling / Pioneer – email
Ian Magruder/ CTEC – email
CTEC of Butte – email
Scott Juskiewicz / Montana Tech – email

File: MiningSharePoint@bp.com – email
BPSOU SharePoint – upload

PIONEER TECHNICAL SERVICES, INC.

# TECHNICAL MEMORANDUM

## Unreclaimed and Insufficiently Reclaimed Sites: XRF to Laboratory Correlation and Regression Analyses and Procedure


**Date:** 6/30/2023

**To:** Mike Mc Anulty

**From:** Scott Sampson, Jackie Janosko, and Maria Pomeroy


# 1 INTRODUCTION

On April 27, 2023, Leslie Gains-Germain and Paul Black of Neptune and Company, Inc. (Neptune) delivered a presentation titled *Passing-Bablok Review and XRF/ICP Regression Analysis* to the Agencies. Statistical methods and the proposed applications of regression analysis for the Unreclaimed (UR) and Insufficiently Reclaimed (IR) sites field X-ray fluorescence (XRF) analytical data (referred to herein as field data) and inductively coupled plasma optical emission spectroscopy (ICP-OES) analytical data (referred to herein as laboratory data) were discussed.

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This memorandum describes Atlantic Richfield Company's (Atlantic Richfield) proposed methodology and application of regression analysis for the UR and IR sites. The proposed methodology is intended to be specifically applicable to site investigations related to the UR and IR projects within the Butte Priority Soils Operable Unit (BPSOU).

# 2 PROPOSED REGRESSION METHODOLOGY AND APPLICATION

## 2.1 Methodology

Among the many regression methods that could be employed for analysis, it is critical to select a method that fits the data and the application. In this case, the intended application is to use regression analysis to predict laboratory concentrations based on field XRF results. For this application, the Neptune team of statisticians recommended the weighted least squares (WLS) method. The paired field and laboratory dataset meets the WLS method assumptions and the WLS method is appropriate for the method applications (i.e., predicting future concentrations).

When determining a regression analysis approach, the selected regression method must match the purpose of the regression application. For example, the Passing-Bablok method and other orthogonal regression methods were developed for the clinical chemistry field to compare two analytical methods. If the data produced by the two analytical methods are analyzed using the Passing-Bablok method and the regression produces a line with a slope of 1 and a y-intercept of 0 falls between the confidence interval bands, the new method was sufficiently similar to the old. For the UR/IR sites, the purpose of the regression method is not to compare the two analytical methods because XRF and ICP-OES do not measure the same quantities (i.e., different sample preparation and analyses techniques). The XRF measures the total metals concentration in a sample, while the ICP-OES measures the environmentally available fraction (EPA, 2008). During the ICP-OES analysis, the soil sample is digested in a solution of nitric acid and the analysis measures the concentration of metals in the acid solution. Therefore, the regression method should not be an orthogonal method, not just because it is already understood that the methods of analyses are not the same, but also because the orthogonal models are not intended for prediction. The types of regression method that meet the purpose of the UR/IR sites include WLS and ordinary least squares.

## *2.2 Application*

The regression analysis will be used to support UR and IR site investigations in two distinct phases. The first will be during the site evaluation phase (Phase I) to determine if field screening of samples using XRF provides reliable data to support remedial decision making and potentially provide justification for adjusting laboratory confirmation limits[1] of future sampling events. The second will be during the site remediation phase (Phase II) to determine the extents of the remediation.

The XRF Field Limits are the XRF concentration values that correspond to the Action Levels for Human Health and Soil Screening Criteria for Waste Identification contaminants of concern described in the BPSOU Consent Decree (BPSOU CD) (EPA, 2020). The statistical analysis of laboratory data and field data will result in regression coefficients, specific to each analyte and model number of XRF used, that can be used to estimate laboratory results from field results. The regression analysis produces a mathematical model that can predict laboratory concentrations that correspond to any future field XRF concentrations together with a 95% certainty interval for laboratory concentration.

Once the regression analysis is complete, the regression model will be used to determine if field screening of samples using XRF provides data that are reliable to support remedial decision making and that XRF Field Limits are chosen to ensure remedial decisions are protective with 95% confidence. For the Phase I work, the lower and upper 95% prediction interval[2] will be used to determine when field teams send samples for laboratory confirmation. For the Phase II work, the lower 95% confidence interval[3] will be used to inform the XRF Field Limits that refine the waste extent boundaries. Table 1 provides an example of XRF Field Limits that could be used during the Phase I and Phase II work. These values are examples only.

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[1] Field teams currently use XRF concentrations equal to ±35% or ±25% of the action level for the Phase I work.

[2] As discussed during the April 27, 2023, presentation, the prediction intervals are the wider bands around the regression line that indicate 95% confidence in the range of future predicted laboratory concentrations.

[3] The confidence intervals are the narrower bands that indicate 95% confidence in future mean laboratory concentrations.

If there are concerns about the XRF Field Limit concentrations being greater than the laboratory action levels during the Phase II work, Atlantic Richfield proposes the following:

- If the lower 95% confidence interval is less than the established laboratory action level, the lower 95% confidence interval will be used as the XRF Field Limit.
- If the lower 95% confidence interval is higher than or equal to the established action level, then the action level will be used as the XRF Field Limit.

The lesser of the lower 95% prediction level and action level concentrations are shown in Table 1.

# 3 Regression Path Forward

The proposed path forward for the regression application and methodology follows:

1. Use the WLS regression method to predict laboratory results from field results.
    a. The datasets will be divided into separate groups for each XRF unit, and an analysis will be conducted to determine if a separate regression is needed for each XRF unit.
        i. For reference, Figure 1 through Figure 5 show the 2018, 2021, and 2022 datasets separated by XRF unit for each of the five contaminants of concerns.[4]
    b. For each year thereafter, a statistical analysis (e.g., a likelihood ratio test, or a t-test for the slope parameter in a separate lines model) will be conducted, for each analyte and each XRF unit used, to determine if newly collected data are equivalent to the previous year's dataset. If the populations are equal, the newly collected data will be added to the previous year's data, and the regression will be updated. If the populations are not equal, a new regression will be performed to determine if the XRF Field Limits are still appropriate.
2. The WLS regression prediction intervals will be used to adjust the XRF Field Limits used to determine which samples to send for laboratory confirmation during the Phase I Work. If XRF concentrations exceed the XRF field limits, the sample is classified as waste.
3. The WLS regression lower confidence interval will be used to confirm the XRF Field Limits for the Phase II work.

## *3.1 Project Submittals Path Forward*

Once Atlantic Richfield reaches concurrence with Agencies, they propose completing the following to proceed with submittal of UR and IR reports:

[4] The regression lines shown in the plots were created using the Microsoft Excel trendlines, which use the ordinary least squares regression method. They are intended to show trends in the data only and will not be used as regression lines in the UR and IR work.

1. Submit a new 2018 and 2021 sampling field to laboratory regression report using the WLS method. This analysis will include UR and IR data.
    a. Response to the previous report comments will not be provided. However, Atlantic Richfield will attempt to address current Agency concerns in the new regression report.
2. Evaluate the 2022 UR and IR data and summarize the analysis and updated regression models in a 2022 regression analysis report.
3. The regression analysis reports will recommend adjusting the positive/negative 25% and/or positive/negative 35% laboratory confirmation sample submittal boundaries and XRF Field limits, where appropriate.
4. Move forward with implementation for Phase II remedial action (RA) using the approved field-delineation method described in the 2022 UR Sites Quality Assurance Project Plan (QAPP) Request for Information (RFI)-01 (Atlantic Richfield Company, 2022), and XRF Field Limits (once Agency approval is received for regression analysis reporting).

# 4 CONCLUSION

There is no uniform regression method that can be applied to any situation. For the UR and IR Sites, Atlantic Richfield proposes using a regression method that fits the decision context. This technical memorandum summarizes Atlantic Richfield's proposed regression model methodology and how it will be used to inform the remedial decisions related to the UR and IR Sites.

# 5 REFERENCES

Atlantic Richfield Company, 2022. Request for Information - 01 to the Butte Priority Soils Operable Unit (BPSOU) Final 2022 Unreclaimed Sites Quality Assurance Project Plan (QAPP). August 31, 2022. Approved by Agencies on November 29, 2022.

EPA, 2020. Consent Decree for the Butte Priority Soils Operable Unit. Partial Remedial Design/Remedial Action and Operation and Maintenance. U.S. Environmental Protection Agency. February 13, 2020. Available at https://www.co.silverbow.mt.us/2161/ButtePriority-Soils-Operable-Unit-Conse. Appendix A to the Consent Decree is the 2006 Record of Decision, Butte Priority Soils Operable Unit Silver Bow Creek/Butte Area NPL Site.

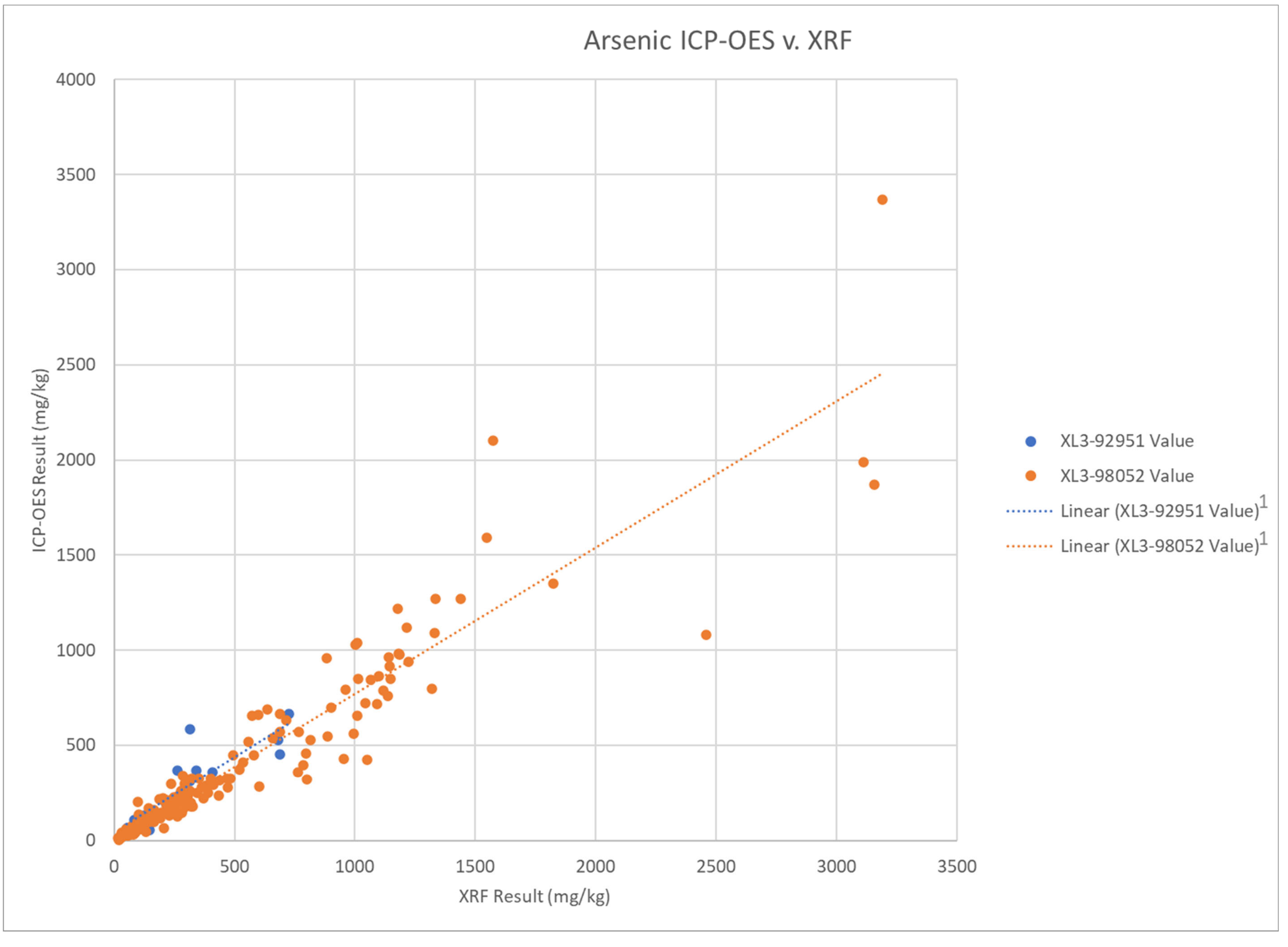
EPA, 2008. X-ray Fluorescence (XRF) Session 3: Representativeness Part 2. Presented on August 11, 2008. Available at https://clu-in.org/conf/tio/xrf_081108/.

# FIGURES

Figure 1. Plot of Arsenic ICP-OES v. XRF Concentrations Separated by XRF Unit

2022 Field Season:

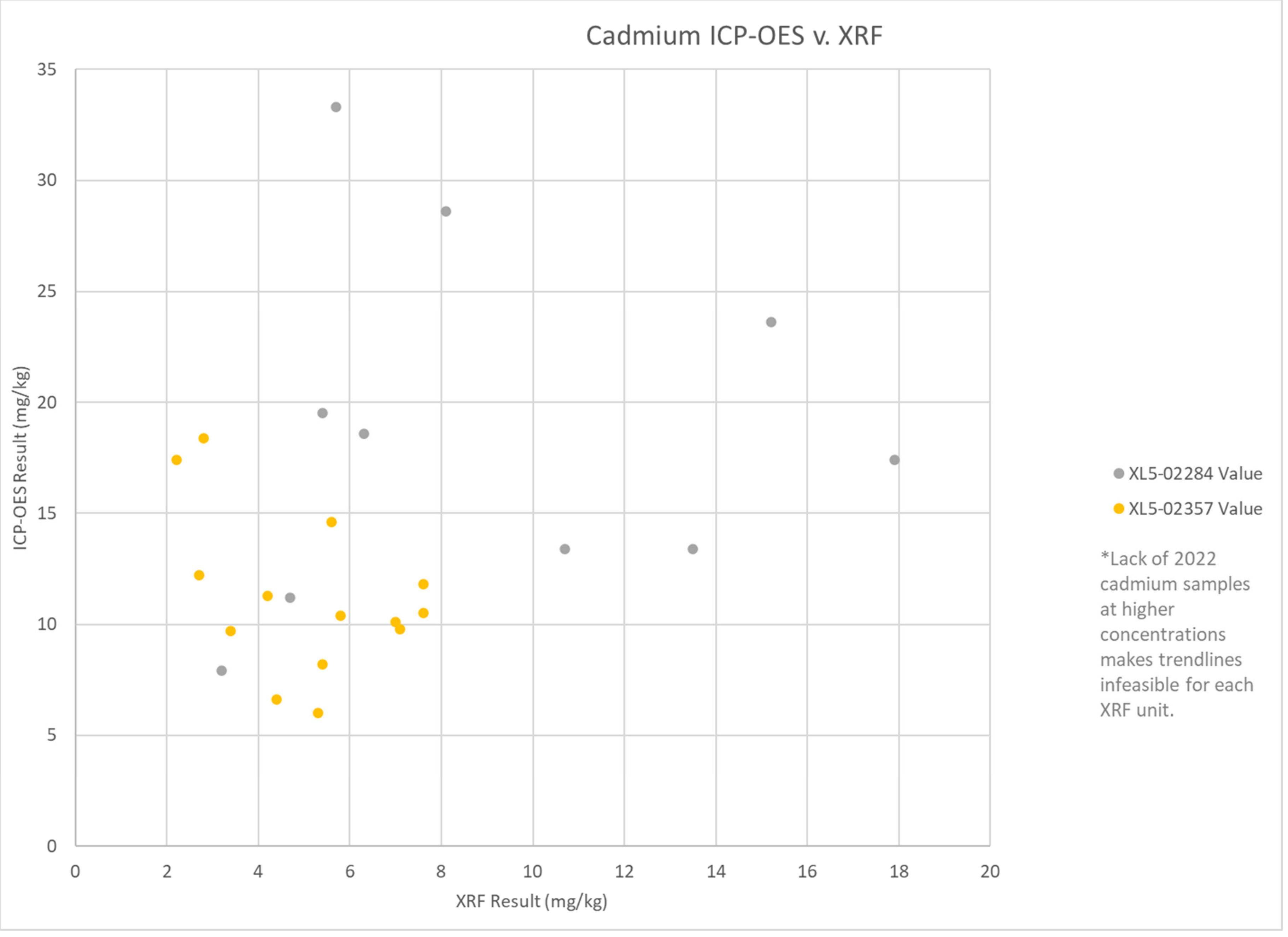

2018 and 2021 Field Season:



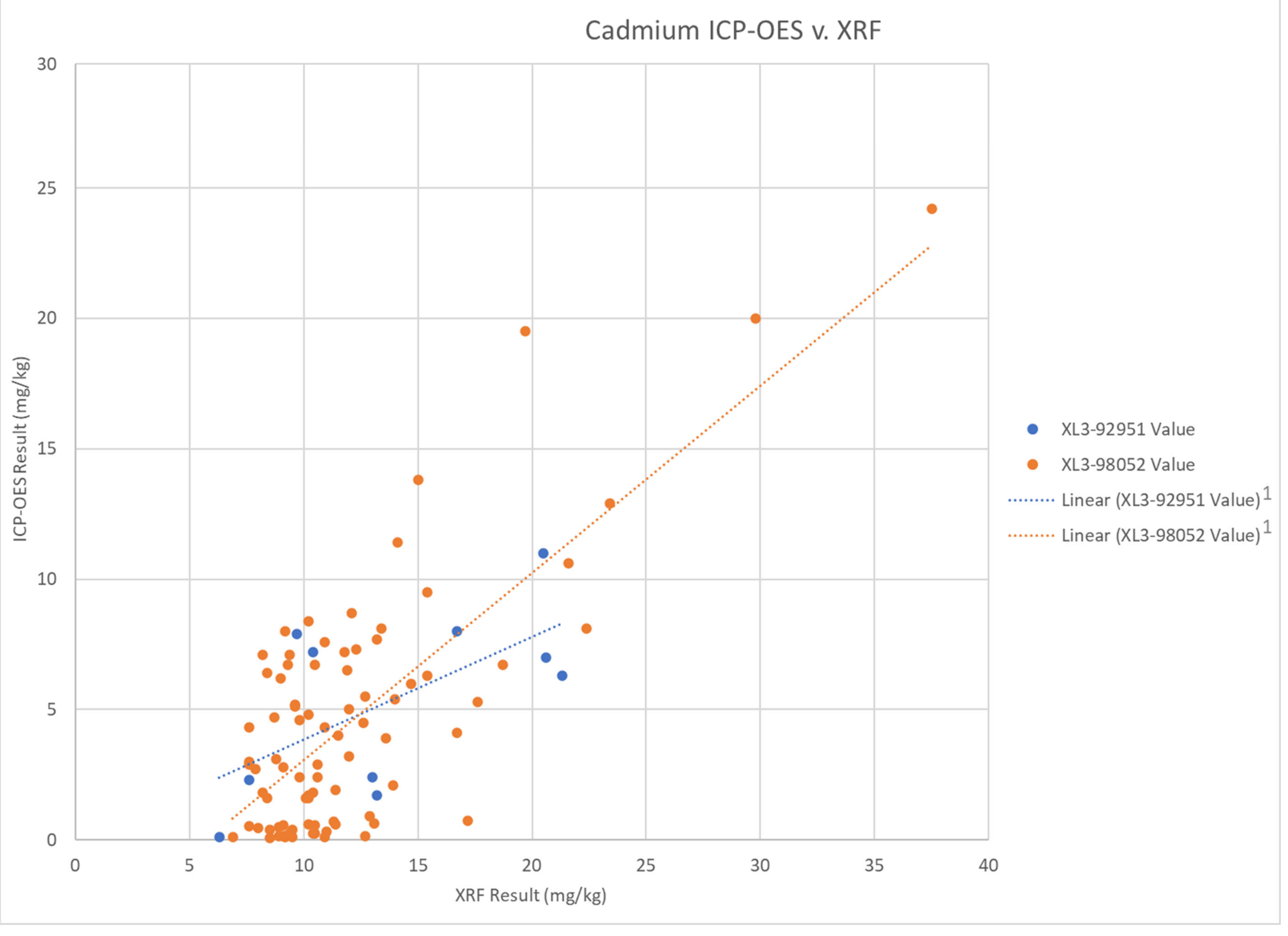

[1]The regression lines shown in the plots were created using the MS Excel trendlines, which use the ordinary least squares regression method. They are intended to show trends in the data only and will not be used as regression lines in the UR and IR work.

Figure 2. Plot of Cadmium ICP-OES v. XRF Concentrations Separated by XRF Unit

2022 Field Season:



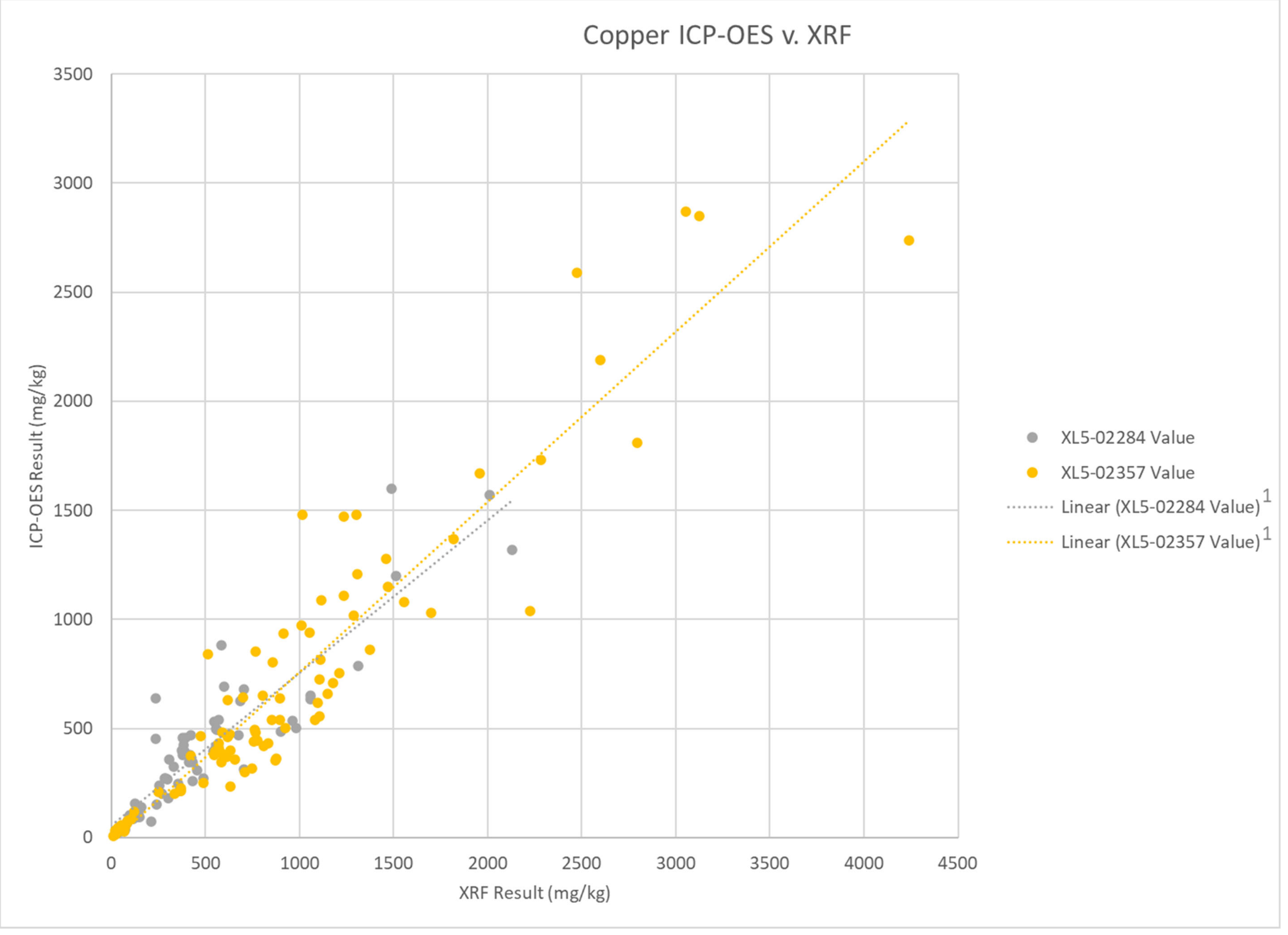

2018 and 2021 Field Season:



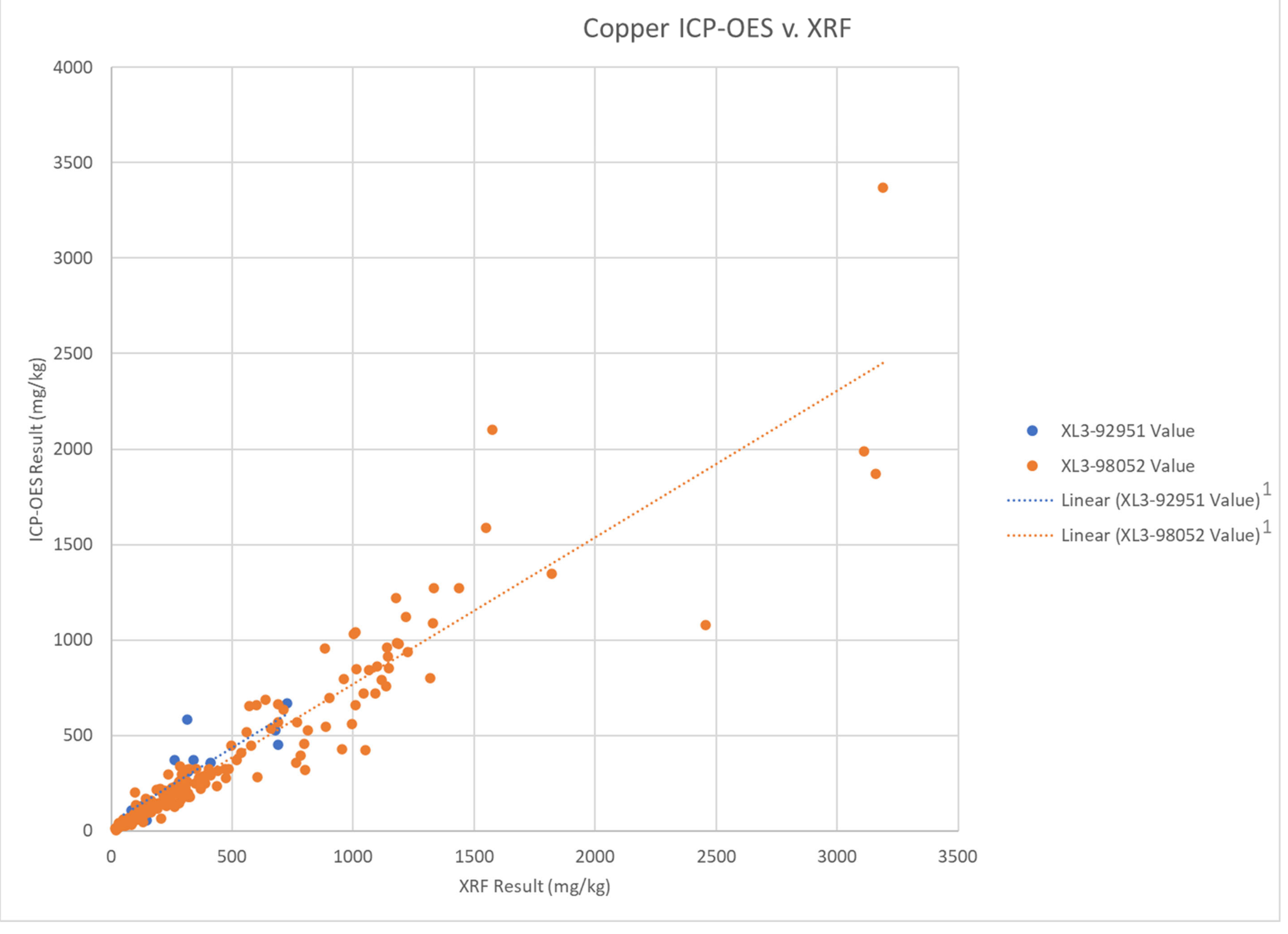

[1]The regression lines shown in the plots were created using the MS Excel trendlines, which use the ordinary least squares regression method. They are intended to show trends in the data only and will not be used as regression lines in the UR and IR work.

Figure 3. Plot of Copper ICP-OES v. XRF Concentrations Separated by XRF Unit

2022 Field Season:



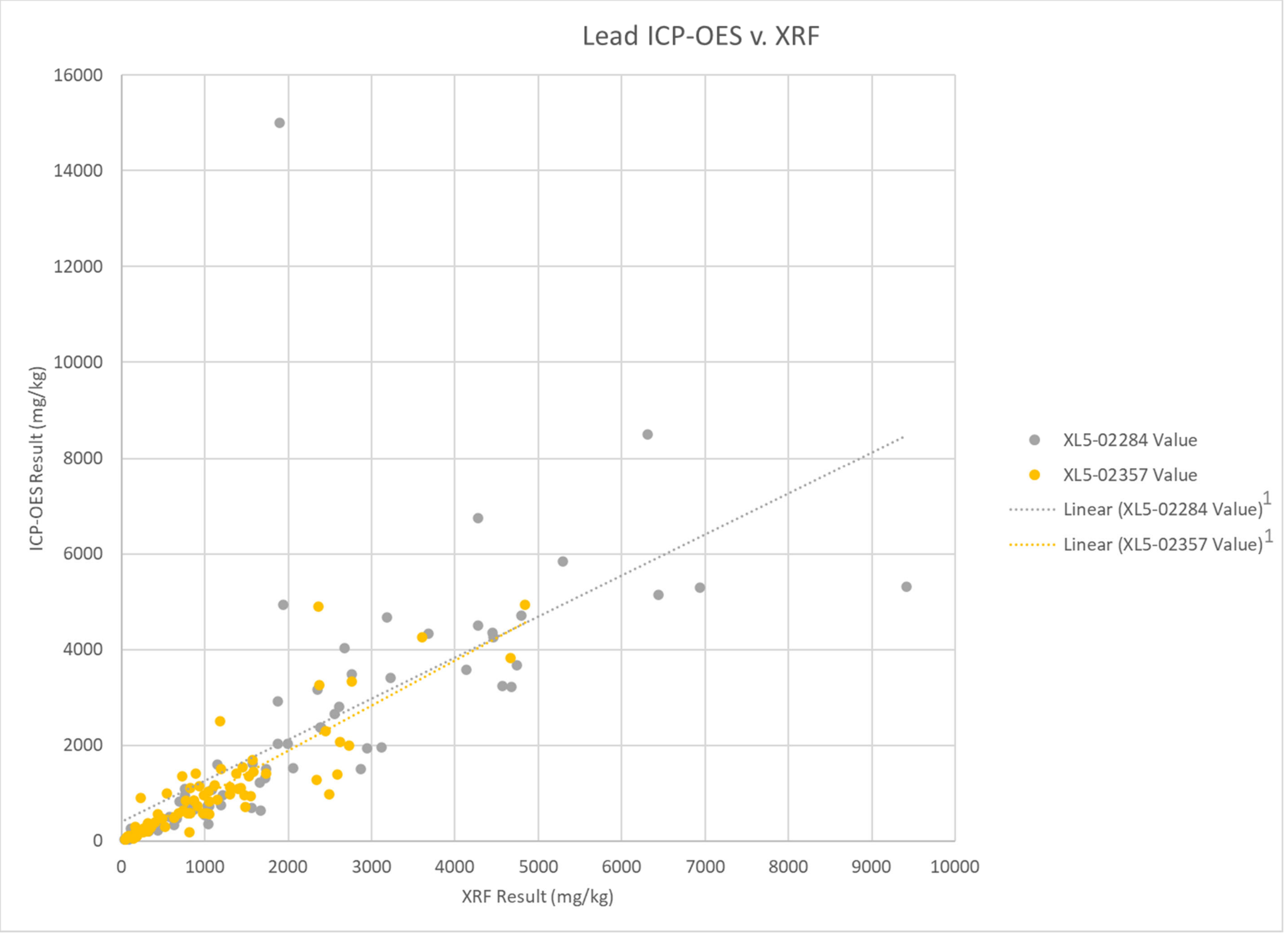

2018 and 2021 Field Season:



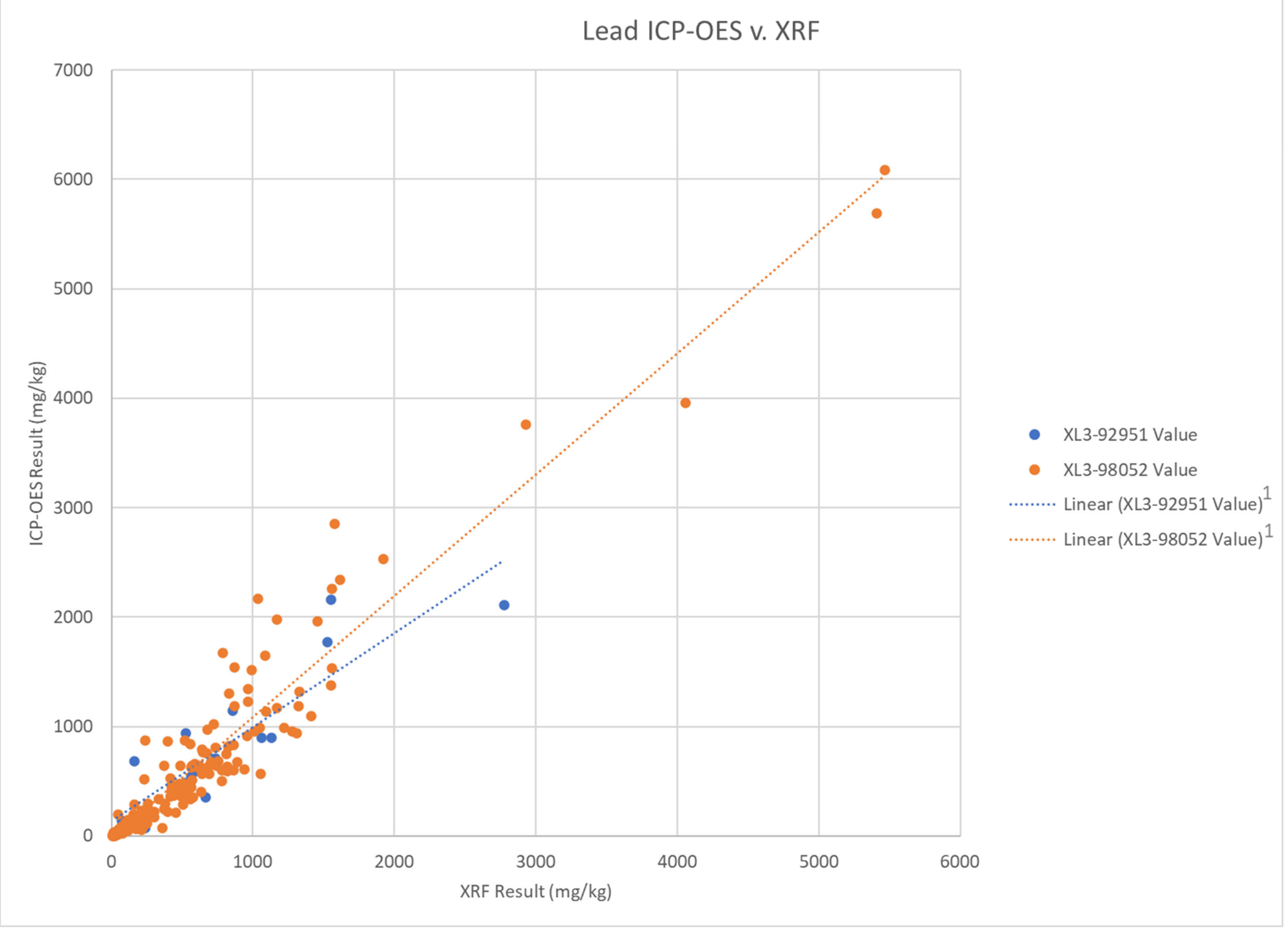

[1]The regression lines shown in the plots were created using the MS Excel trendlines, which use the ordinary least squares regression method. They are intended to show trends in the data only and will not be used as regression lines in the UR and IR work.

Figure 4. Plot of Lead ICP-OES v. XRF Concentrations Separated by XRF Unit

2022 Field Season:



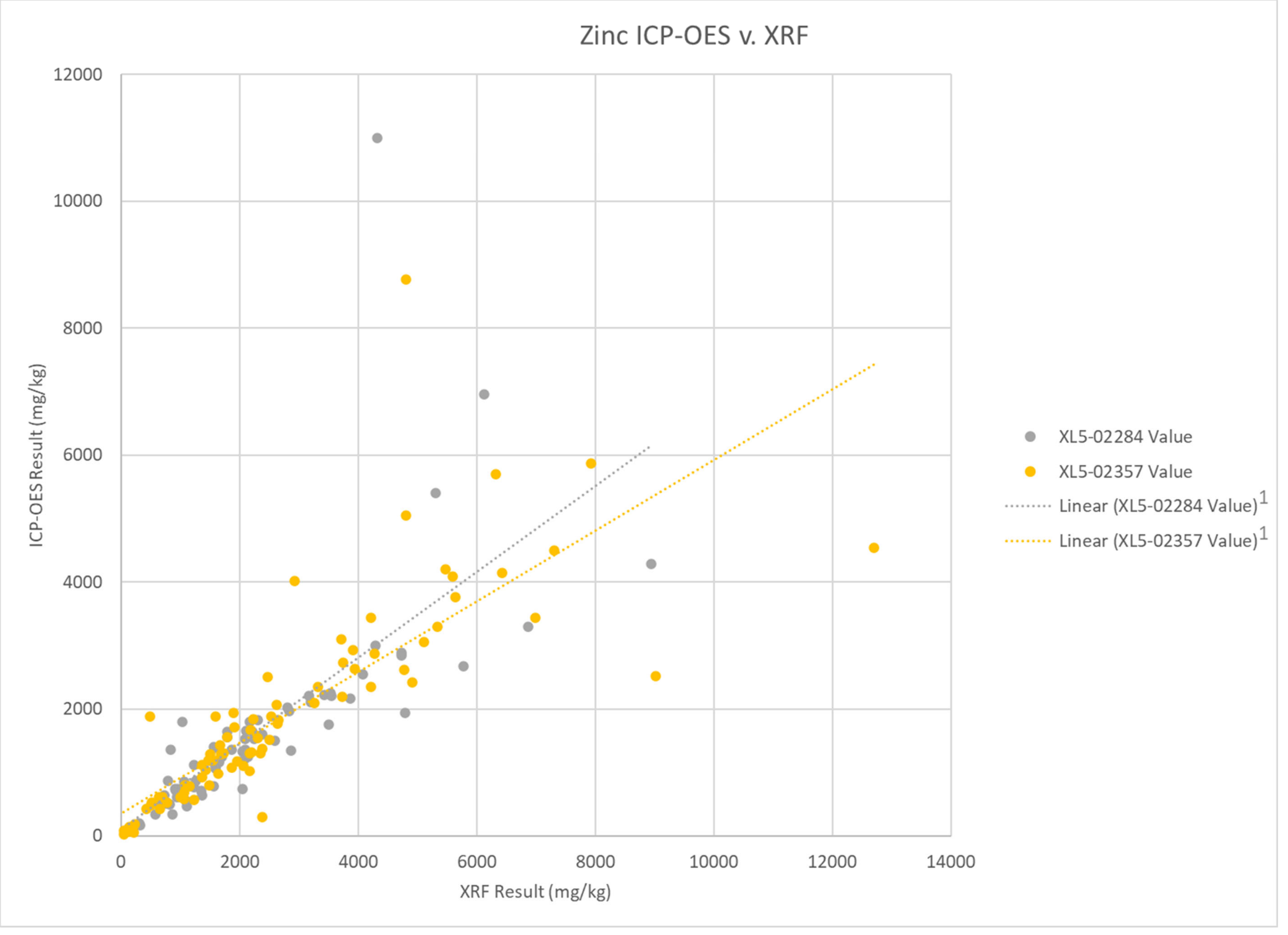

2018 and 2021 Field Season:



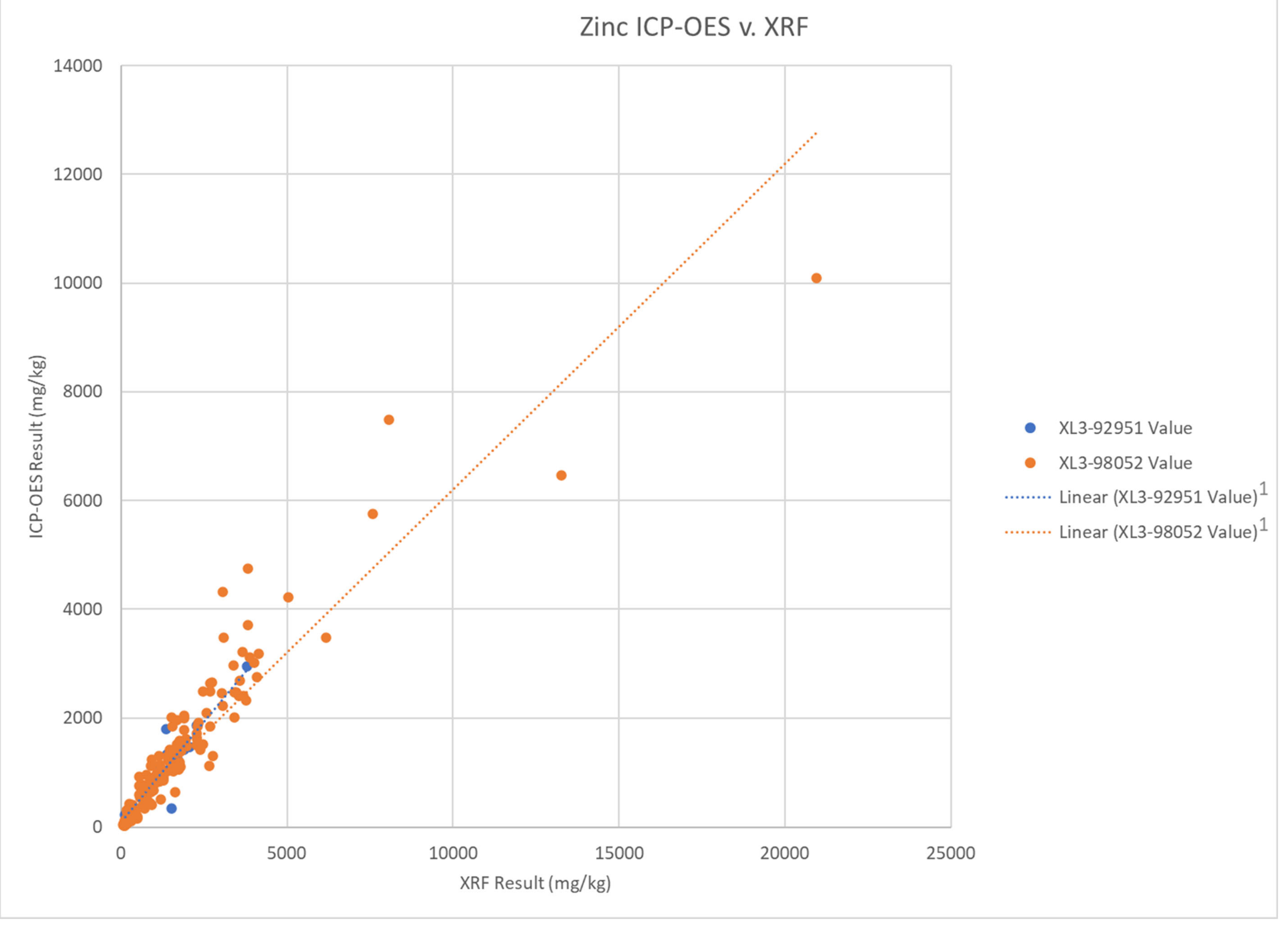

[1]The regression lines shown in the plots were created using the MS Excel trendlines, which use the ordinary least squares regression method. They are intended to show trends in the data only and will not be used as regression lines in the UR and IR work.

Figure 5. Plot of Zinc ICP-OES v. XRF Concentrations Separated by XRF Unit

2022 Field Season:




2018 and 2021 Field Season:




[1]The regression lines shown in the plots were created using the MS Excel trendlines, which use the ordinary least squares regression method. They are intended to show trends in the data only and will not be used as regression lines in the UR and IR work.

# TABLES

Table 1. XRF Field Limits Derived from Proposed XRF to Laboratory Regression Analysis

Table 1. **Example** XRF Field Limits Derived from Proposed XRF to Laboratory Regression Analysis[1]

| | | | Phase I | | | | | | Phase II[4] | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Lower Lab Confirmation Limit | | | Upper Lab Confirmation Limit | | | | |
| **Action Level** | **Type** | **Value** | **Current: Value -25% (IR Sites)** | **Current: Value -35% (UR Sites)** | **WLS Regression LPL** | **Current: Value +25% (IR Sites)** | **Current: Value +35% (UR Sites)** | **WLS Regression UPL** | **WLS Regression LCL** | **Lesser of the Action Level and LCL[4]** |
| Arsenic - Recreational | Human Health[2] | 1,000 | 750 | 650 | **891** | 1,250 | 1,350 | **2,208** | 1,215 | **1,000** |
| Arsenic - Commercial or Industrial | Human Health[2] | 500 | 375 | 325 | **440** | 625 | 675 | **1,127** | 609 | **500** |
| Arsenic - Residential | Human Health[2] | 250 | 188 | 163 | **214** | 313 | 338 | **586** | 306 | **250** |
| Arsenic – Waste Identification Criteria | Waste ID[3] | 200 | 150 | 130 | **169** | 250 | 270 | **478** | 246 | **200** |
| Cadmium – Waste Identification Criteria | Waste ID[3] | 20 | 15 | 13 | **26** | 25 | 27 | **55** | 34 | **20** |
| Copper – Waste Identification Criteria | Waste ID[3] | 1,000 | 750 | 650 | **837** | 1,250 | 1,350 | **2,417** | 1,185 | **1,000** |
| Lead – Non-Residential | Human Health[2] | 2,300 | 1,725 | 1,495 | **1,510** | 2,875 | 3,105 | **3,529** | 2,058 | **2,058** |
| Lead – Residential | Human Health[2] | 1,200 | 900 | 780 | **726** | 1,500 | 1,620 | **1,976** | 1,073 | **1,073** |
| Lead – Waste Identification Criteria | Waste ID[3] | 1,000 | 750 | 650 | **583** | 1,250 | 1,350 | **1,694** | 894 | **894** |
| Zinc – Waste Identification Criteria | Waste ID[3] | 1,000 | 750 | 650 | **808** | 1,250 | 1,350 | **2,154** | 1,235 | **1,000** |

[1] All values are in mg/kg. Note that values presented are examples only.

[2] From EPA Record of Decision Amendment (RODA) BPSOU, Table 2-1 (EPA, 2020)

[3] From BPSOU CD, Appendix D Table 1, Waste Identification Criteria (EPA, 2020)

[4] For the Phase II work, if there are concerns about using an XRF Field Limit greater than the Action Level. Shown below is the lesser of the Action Level and Lower Confidence Level.

Acronyms: WLS: weighted least squares; mg/kg: milligrams per kilogram; LPL: lower prediction level; LCL: lower confidence level

| | |
|---|---|
| **Value in Bold** | Example XRF Field Limit |
| (highlighted cell) | Current lab confirmation interval insufficient per LPL of WLS regression for 2018/2021 UR Data. Samples with concentrations between Value-25% and LPL may need to be re-evaluated to estimate if the sample passes or fails the action level once the regressions for each XRF unit are complete. |