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D. I1.2.3. Correlation report of characterization studies based on information from geophysical investigations and traditional investigations

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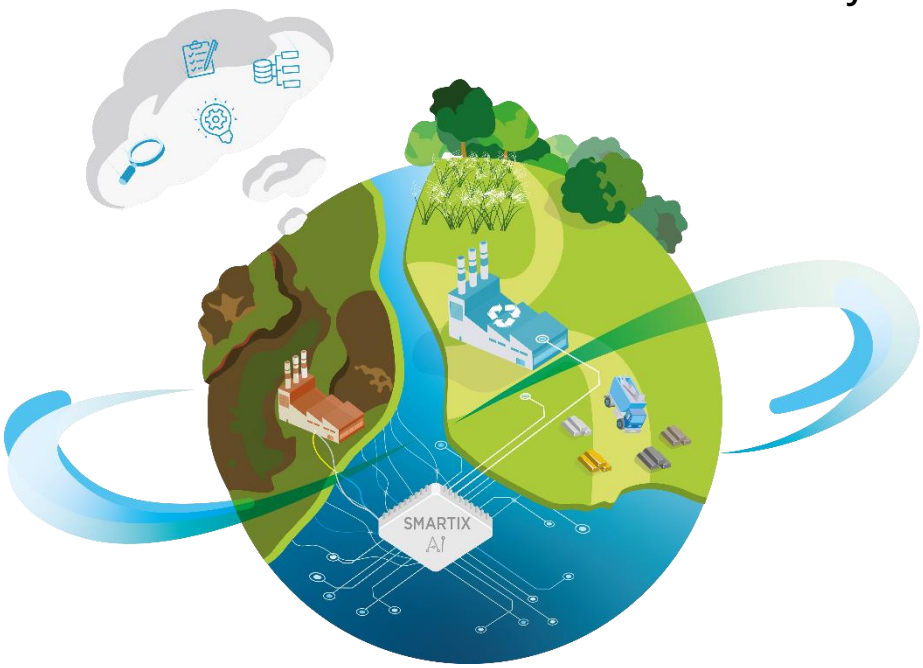
Version 1.0



SUMMARY

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This brief report analyses the correlations observed using rapid assessment tools, geophysical characterisation and traditional laboratory analyses.

This report is submitted in fulfilment of the requirements of work package I1

1 INTRODUCTION

The NWE-REGENERATIS project (Interreg North-West Europe) aims to recover (metals, minerals, and land) from PMSDs using urban mining methods and valorise the site. Three pilot sites were selected one of which was the former integrated steelworks at Teesside.

As an integrated steelworks which processed from raw materials to finished product there was several know areas used for the storage of waste products dating back as far as the 1900s.

The significant areas of previous industrial activity are those of the Redcar works complex (comprising the blast furnace, coke ovens, sinter plant and materials handling areas), the Lackenby steelmaking complex (comprising the basic oxygen steel and continuous casting plants), the Grangetown Prairie (site of the Cleveland Iron Works), the zone designated as Landfill and Waste Management Facilities (comprising the SLEMS waste management facility, the High Tip Landfill and a metals recovery area) and the South Bank zone (site of the Clay Lane furnaces and the South Bank Coke Ovens).

Samples were taken from site for chemical analysis, laboratory testing, material separation testing, pyrometallurgical testing and hydrometallurgy.

2 SELECTION OF AREA FOR GEOPHYSICAL INVESTIGATION

A number of areas were identified for consideration all of which have been used for waste management. These are shown in Figure 1.

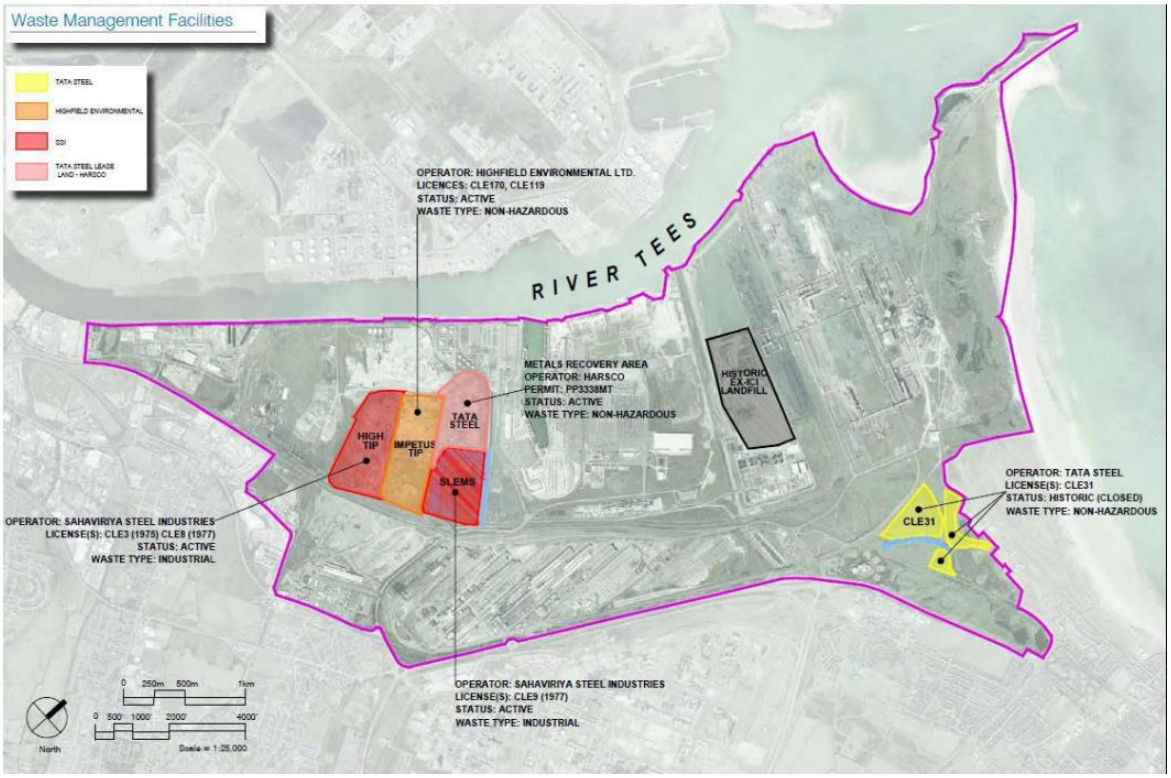


Figure 1. Waste management facilities within PMSD-I1 Teesworks.

Due to the development of the site, an area termed CLE31 was selected for the geophysical study at the Teesworks site.

CLE31 (Figure 2) is a closed waste disposal site and was used primarily for the disposal of blast furnace and steelmaking slag with a small percentage of general site waste. The site was used from the 1930s until it was closed in 2002.

Figure 2. CLE31 landfill site

3 CLE31 ANALYSIS

Geophysical investigations were carried out on CLE31 from May 17th to May 25th, 2022. During the measurement campaign several samples were taken from locations associated with the geophysical measurements. A total of 17 samples collected from both the surface and sub-surface (total of 34x samples), 3x replicates were taken at each location. These were split and taken by Cranfield University, BRGM and Materials Processing Institute.

The results from the geophysical survey are provided in D.I.1.2.1. The results of the detailed analysis of samples are provided in D.I.1.2.2.

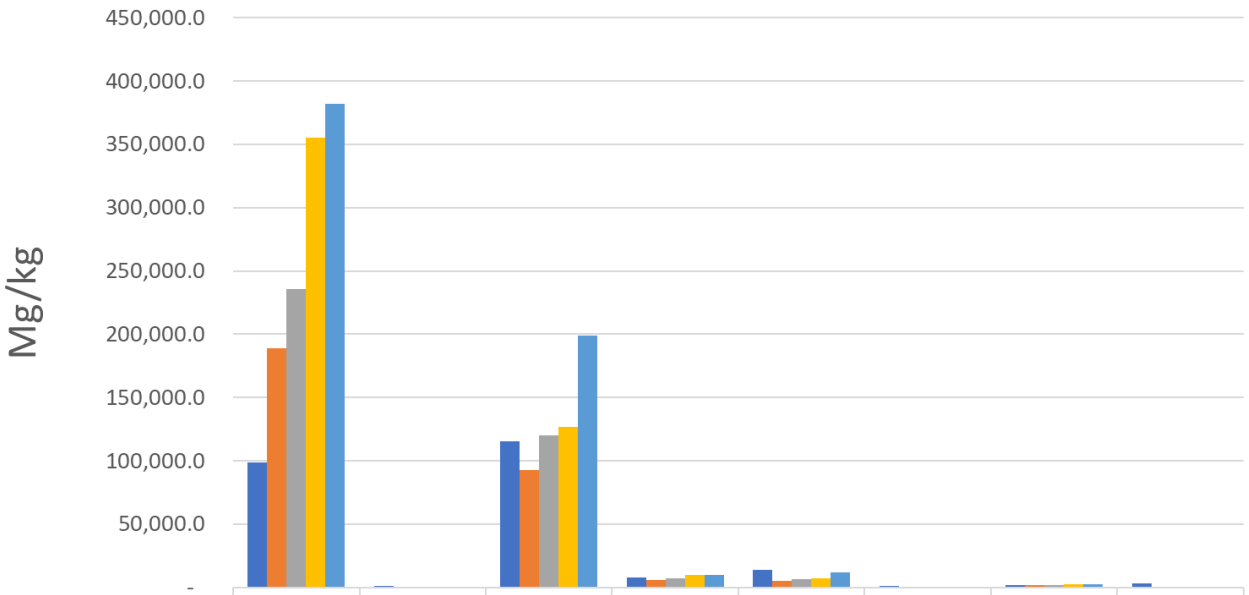
Samples were collected from the surface and sub-surface (~20cm depth) of 17 locations (34 samples) and selected to overlap with geophysical measurements and capture the full range of conditions observed on-site and through initial geophysical measurements. Deliverable 1.2.3 presents the correlation of rapid assessment methods with conventional techniques.

Samples underwent 5 sample treatment steps; sieving to <2 mm; drying at 105°C for 24 hours (ISO 11465:1993); transfer to portable X-ray fluorescence spectrometry (pXRF) sample cups; grinding with a disk mill for 18 seconds to produce a fine powder; and ignition at 450°C for 4 hours to remove organic matter (BS EN 13039:2000).

Before and after each sample treatment step replicate pXRF measurements were taken using a Delta Premium (Olympus USA) with Rh X-ray tubes in soil mode using the steal suitcase accessory.

Following pXRF measurements, all samples underwent microwave-assisted acid digestion following (ISO 11047:1998). Briefly, 0.5 g of sample was dissolved in Aqua regia (HCl: NHO_4, 6 mL:2 mL Fisher Brand, UK) followed by the standard microwaving program. after cooling digestate was filtered and diluted in deionised water in volumetric flasks (100 mL) and stored at room temperature until analysis by induction coupled plasma-mass spectrometry (ICP-MS) (PerkinElmer NexION 350D).

An overview of the metals analysis following ICP-MS and portable XRF are shown in Figure 3.



	Ca	Cr	Fe	K	Mn	Ni	Ti	Zn
ICP	98,875.3	835.2	115,591.	7,434.9	13,710.8	997.7	1,498.3	3,086.1
XRF Sieved	188,708.	266.5	92,960.1	5,626.3	5,186.9	35.3	1,443.6	150.5
XRF Dried	235,463.	327.0	120,327.	6,838.1	6,158.7	42.1	1,839.7	183.8
XRF Ground	355,031.	352.9	126,726.	9,637.3	7,172.8	48.7	2,299.6	192.2
XRF Post-ignition	382,253.	634.8	198,913.	9,756.7	11,869.6	169.4	2,432.8	112.4

Figure 3. Metals analysis of CME31 samples using ICP-MS and pXRF.

All data analysis of ICP-MS and pXRF results was carried out in R using the tidyverse packages. For the correlation of geophysical and ICP-MS data geophysical measurements were extracted for each sample using GPS data.

4 CORRELATION ANALYSIS

4.1 ICP-MS AND ELEMENTAL DISTRIBUTION

ICP-MS was used as the gold standard method to evaluate pXRF and geophysical methods. Across all 26 elements measured with ICP-MS, only 9 were above the Limit of detection (LOD) shown in Figure 1. The most prevalent elements were Fe and Ca at an average of 11.8 and 9.8 %w/w respectively followed by Mn>K>Zn>P>Ti>Ni and Cr with average concentrations ranging between 13711 and 835 mg kg^{-1}. Hg, Co, Cd, As, Sb, Sc, Rh, Ge, Bi, Ag, Mo, Sr, Se, Pb, Cu, and Ba were all below the LOD of 200 mg kg^{-1}.

Measured concentrations of Fe were similar to those observed in CRM of BOS slag (BAS-CRM-381 ECRM-879-1 https://www.basrid.co.uk/) as were Ti and Mn. But Cr, P and Ca were substantially different with Ca being a third of the value reported in the CRM (30% w/w) these discrepancies may be attributed to the mobility of elements in the environment as the slag weathered.

Fe Ca Mn Ti and Cr all had bi-modal distributions this is likely due to the two observed matrixes at the site with samples showing lower Fe Ca Mn Cr and higher Ti being composed of the capping soil rather than BOS slag.

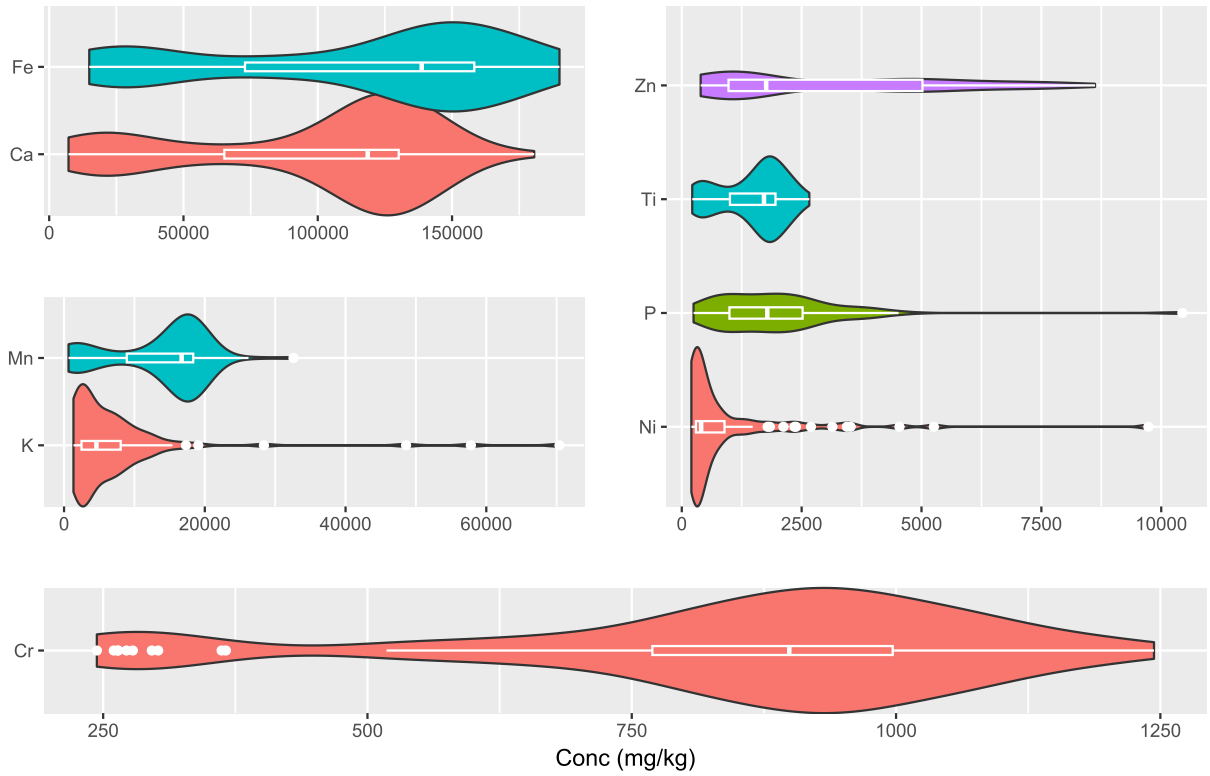


Figure 4. Violin plot showing the range and distribution of ICP-MS measurements for samples collected from CLE32 (Teesside, UK).

4.2 INVESTIGATION OF SAMPLE PRE-TREATMENT AND PXRF'S ACCURACY.

To assess the precision of pXRF after each treatment step relative standard deviation (RSD) was calculated from the 6 replicate measurements of each sample (Figure 5). Raw untreated samples showed the highest RSD consistently reaching >25%, but sieving brought the majority of measurements under 25% RSD. Drying and changing the sample vessel to pXRF sample cups made limited difference to the average RSD, but drying did reduce outlier values to <60% RSD.

Grinding made the most substantial difference reducing results less than 10,000 mg/kg to <10% RSD but measurements over 10,000 mg/kg remained higher at <25%. Igniting samples made no further improvement in precision. ICP overall showed low RSD <10% but for elements Ca, P, Ti and K, ICP was less precise than ground pXRF with RSDs of more than 10%.

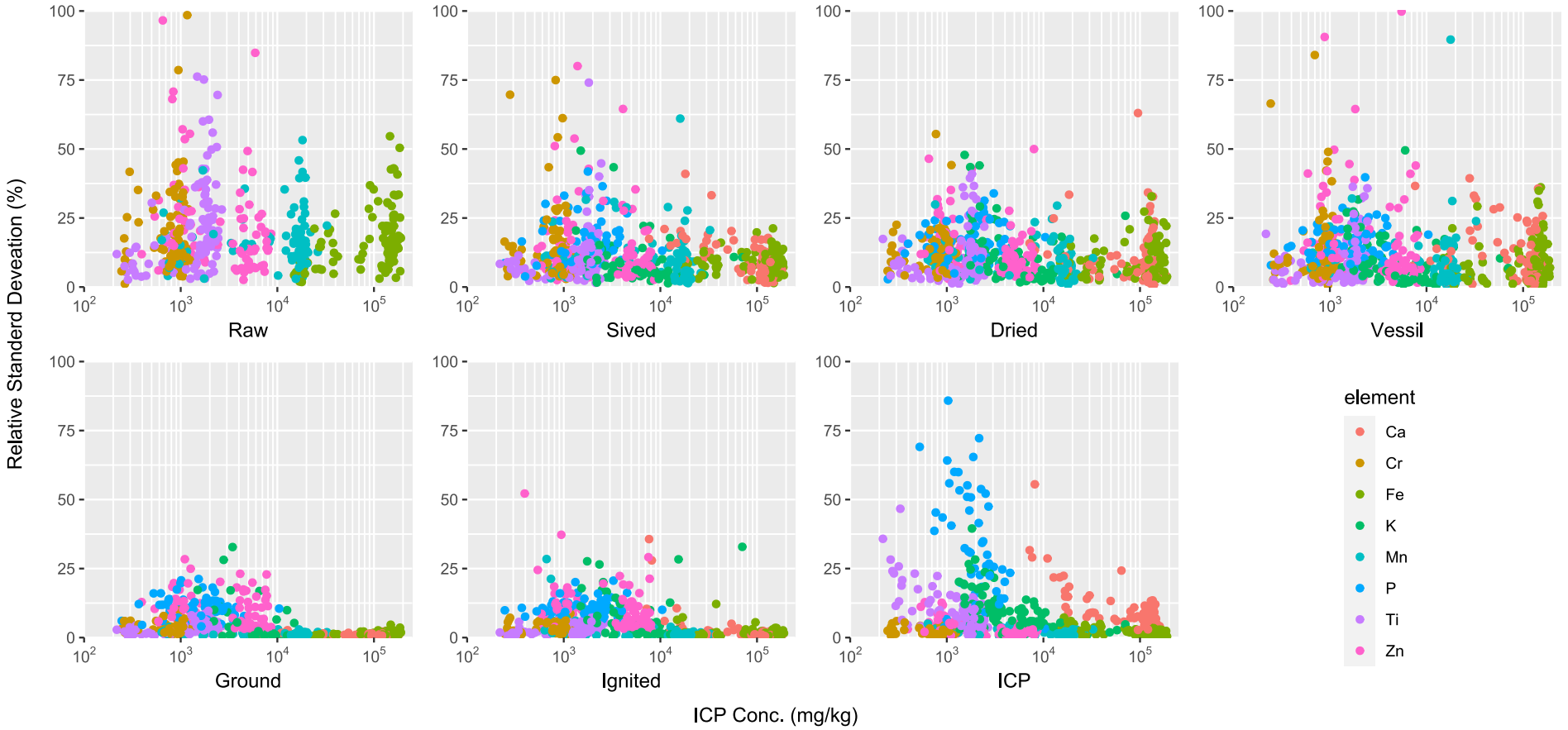


Figure 5. Relative standard deviation for pXRF measurements at each stage of sample treatment

To assess the accuracy of pXRF after each treatment step pXRF results were correlated against ICP-MS measurements (Figure 3). pXRF did not show a strong correlation for raw samples having a R^2 value of 0.66. But once samples were sieved this rose to 0.72 and continued to rise with each sample treatment to a maximum of 0.88. Despite ground and ignited samples having the highest R^2 they did not have gradients closest to 1 which was observed in the dried and pXRF sample cup steps 0.996x and 1.03x respectively. This either means pXRF is over reporting or ICP is under reporting values. Further analysis of certified reference materials would need to be carried out to verify which instrument is miss reporting.

Based on these results we can determine that samples would need to be sieved and dried to meet EPA quantitative screening level (R^2>0.7 and RSD <20%) for Ca Fe and Ti. But for Ca Fe and Ti samples would need to be ground to meet EPA definitive level (>0.85 and RSD <10%) while Zn, P, Mn, K, Cr would only reach EPA quantitative screening level after grinding.

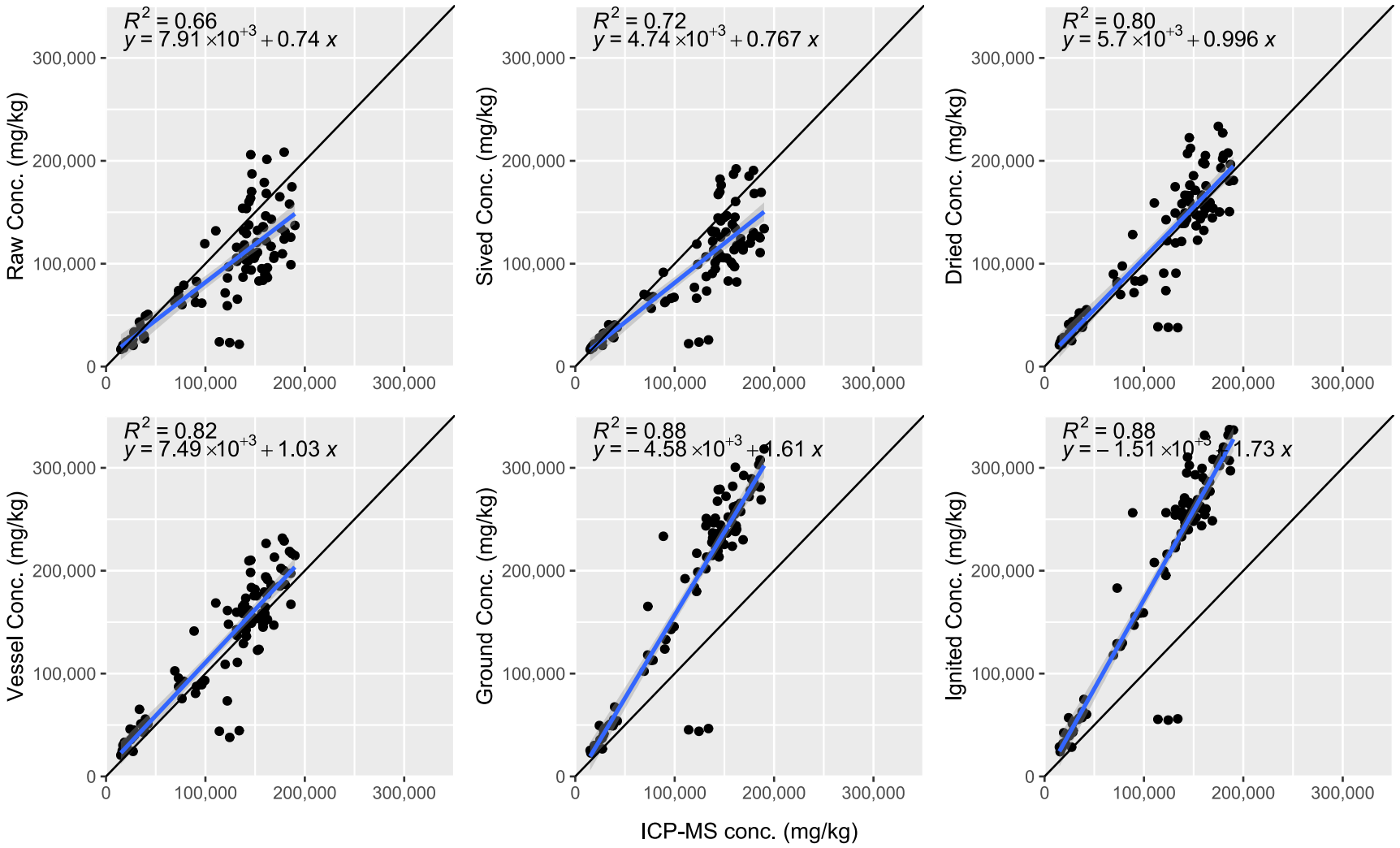


Figure 6. correlation of ICP-MS (x-axis) and pXRF (y-axis) measurements of Fe after each stage of sample treatment, the black line represents a perfect 1 to 1 relationship blue line represents line of best fit.

4.3 Correlation of ICP-MS and Geophysical Data

Of the four methods of geophysics deployed at Teesside electrical resistance tomography (ERT) and electromagnetic induction (EMI) were selected for correlation analysis with ICP-MS. ERT in both resistivity and changeability modes resulted in R^2 values of <0.01 to 0.22 with one outlier of .46 across all 9 elements (Figure 4). For EMI in conductivity and inphase signal using both PRP and HCP modes, R^2 values ranged between <0.01 and 0.53. of the 4 different modes. conductivity-PRP showed the highest R^2 with an average of 0.30 across the 9 elements (Figure 4).

Despite variance in R^2 values across 9 elements and 6 geophysical methods, no correlation was observed disproving the hypothesis that EMI/ERT and surface sample ICP-MS measurements from Teesside will positively correlate with an r^2 value of >0.7. Therefore, these measurements cannot be combined with surface sampling to create a rapid low-cost method of post-metallurgical site surveying. However, it does not disprove the hypothesis that EMI/ERT and borehole sample ICP-MS measurements from Teesside will positively correlate with an r^2 value of >0.7.

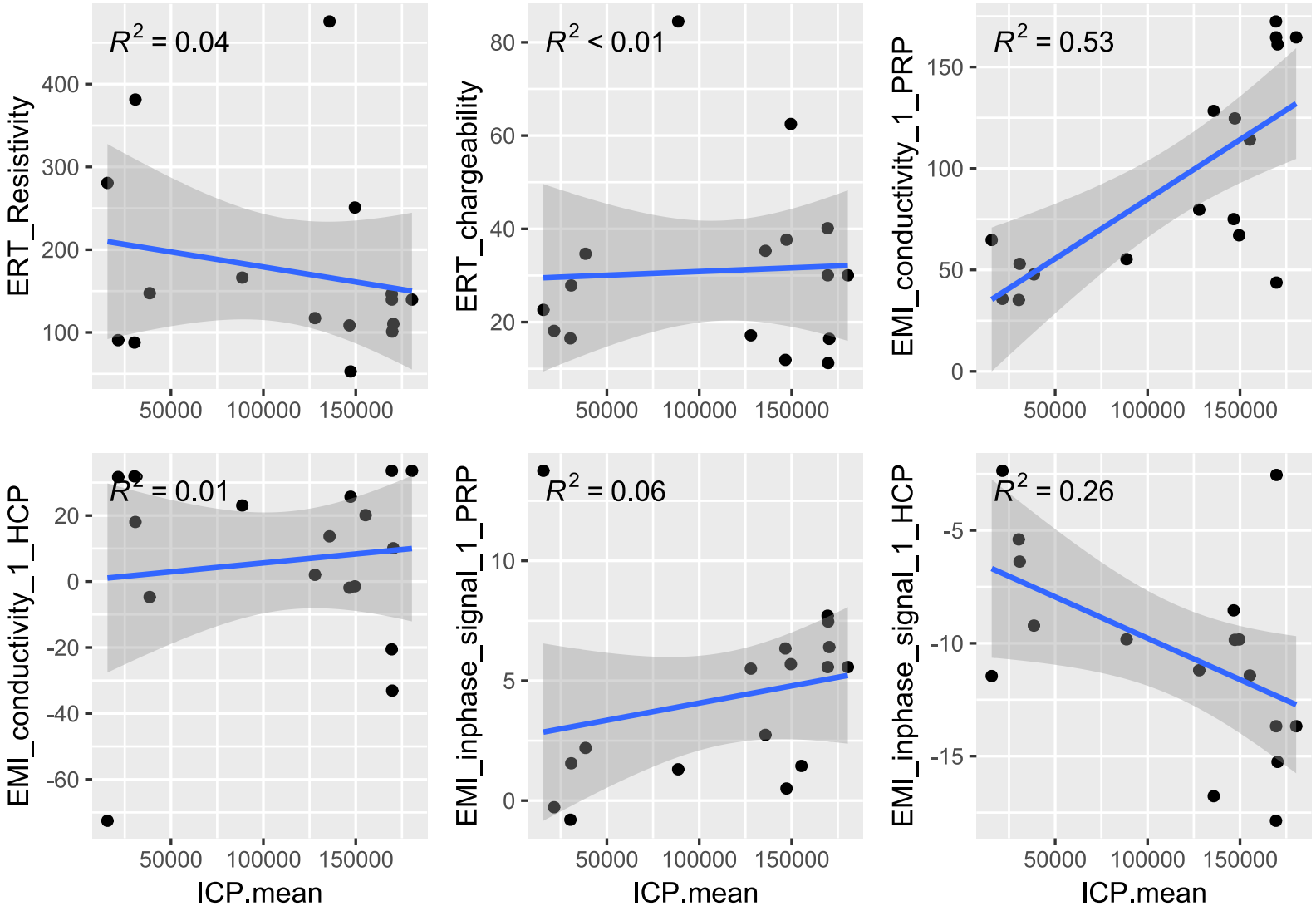


Figure 4: Correlation of Fe ICP data with ERT (2 modes) and EMI (4 modes) measurements.