Portable XRF and wet materials: application to dredged contaminated sediments from waterways

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ABSTRACT: The sustainable management of dredged waterway sediments requires on-site determination of the main pollutants to facilitate their safe reuse or treatment. Portable X-ray fluorescence (pXRF) is commonly used for similar applications with contaminated soil, but the high water content of dredged sediments precludes any application of standard methods. Measurements for Pb, Zn, Cu and As were performed on-site on raw wet sediments with 50 to 70% water contents during dredging or mapping operations. These results, although two or three times lower than laboratory analyses on the same samples, were found to be related to absolute concentrations closely enough to rank samples. In order to investigate further the feasibility of field analyses on wet sediments, partial dehydration methods were tested. The most efficient technique is based on a hand press. It is simple and quick enough to be used on dredging boats during operations and produces sample pellets with 30 to 50% water contents. The relationship between pXRF measurements on these pellets and laboratory analyses was found to be sufficiently linear to calculate estimated concentrations. Potential differences were found to be less than 20% for Pb and Zn. Higher differences for Cu were due to very low concentrations, within twice the limit of detection (LOD). Some limitations were observed. The water content in pellets is variable depending on the sediment type or matrix. The correction factors vary between the measured elements and they may also vary with matrix chemistry. However, Pb-Zn-Cu-As concentrations were ranked and evaluated accurately and the geochemical signatures of the samples were preserved.

We demonstrated that, with a simple partial dehydration procedure, pXRF measurements can be reliably related closely enough to absolute concentrations to make field decisions for sediment management. Since the approximately linear relationships between measurements on semi-wet samples and laboratory analyses are matrix- and site-dependent, they must be recognised before using pXRF on wet samples for decision making.

KEYWORDS: *portable XRF, water, moisture, contaminated sediments, waterways, dredging*

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INTRODUCTION

Environmental applications of portable X-ray fluorescence spectrometry (pXRF) were developed for soil as early as the 1990s (Shefsky 1995). These applications have been validated by the development of the EPA 6200 standard method (US-EPA 2007). Matrix similarity with waterway or harbour sediments suggested the scope of pXRF could be extended to these measurements (Kirtay *et al.* 1998; Plater *et al.* 1999). However, this development has faced difficulties due to a much broader range of water contents in sediments. It was soon demonstrated that water contents above 20% in soil or sediment could be a major source of error on absolute results (US-EPA 2007), but neither the type of error nor its relationship with water contents were investigated. It was only recommended to dry the samples before measurements.

Some applications of pXRF are based on the ability to provide immediate measurements, without waiting for drying. Examples of such applications occur during contaminated site remediation operations. The term 'measurement' is used deliberately instead of 'analysis', since absolute accuracy is not mandatory for decision-making. Sensitivity and reproducibility are more essential for most decisions. The incorporation of such measurements in the data-set supporting a decision is possible, provided that the level of uncertainty is properly quantified. This was successfully implemented in the Dynamic Sampling Plans (Robbat 1997), ASAP (US-DOE 2001) and Triad (Crumbling 2001) approaches to decision-making.

Sediments accumulate over time in canals and other waterways. They comprise eroded soil, industrial or urban muds and wastewater-derived solids. Periodic dredging is required to maintain navigability. Waterway sediments are often contaminated by a wide range of potentially toxic substances, a legacy of the industrial history and urbanisation (Martin 2004; Laboudigue *et al.* 2011). Among these substances, heavy metals and metalloids (atomic mass > 39) can be determined by pXRF. This method can operate in rough field conditions and with basic training of local staff without compromising the quality of results (Higueras *et al.* 2012).

Sediment dredging and management may benefit from immediately available measurements in several ways (Lemière *et al.* 2012a, b): during sampling operations aimed at the preliminary characterisation of a canal section to be dredged; during dredging operations, at the dredging site or on the boat; after dredging operations, while entering the treatment facility; and after dredging operations, while unloading at the sediment reuse site. In all these situations, the sediment samples have water contents typically between 30 and 70% (Dalmacija *et al.* 2006; unpublished data by VNF (French Inland Waterways) and SPW (Public Service of Wallonia)).

However, it may be impractical to dry samples on-site. Measuring the water content on-site is not an easy alternative either: sediments are too fluid for humidity sensors based on pin electrodes or too absorbent for infrared techniques due to their high organic matter content.

The purpose of the present study was to: (1) investigate the relationship between water content and measurement reliability; (2) identify practical and reproducible field techniques for drying sediment samples to standard water content, and; (3) establish a viable compromise between measurement quality, handling time and practicality.

The robustness, low cost and performance characteristics of pXRF spectrometers enable easier, more flexible operation and more widespread availability in dredging operations than any other instrument.

MATERIALS AND METHODS

Sample types and preparation

On-site analysis of waterway sediments by pXRF was performed at various occasions during 'GeDSeT', a research project on sediment management (Laboudigue *et al.* 2011; Lemière *et al.* 2012b). Portable XRF was therefore used on-site for pollutant characterisation before dredging, during dredging operations, at sediment disposal sites on land and during sediment remediation pilot tests.

The evaluation of the suitability of pXRF for waterway sediments was one of the objectives of the project and pXRF testing was performed routinely alongside most project activities. As a consequence, the sample sets studied here are not homogeneous and the results discussed in the present paper were obtained through the comparative analysis of tests carried out during campaigns in several different locations and situations, rather than through a straightforward experimental plan.

Sediment samples for pollutant characterisation before dredging were collected using a hand auger (Figure 1). They were processed, partly dehydrated and analysed on-board the boat used by SPW (Public Service of Wallonia). Dehydration was performed by manual hand-pressing in tissue paper (2010 campaign) (Figure 2) or using a filter press device (2011 campaign) (Figure 3a and b). The filter press was developed by the pXRF manufacturer to deal with wet samples or sludge. Pressure is gradually increased by hand in order to allow a progressive release of water. It can be operated under any field conditions, without electricity, and allows short delays (5 to 10 min) between sampling and analysis. For these reasons, it was preferred to Büchner filtration and to induction heating.

Sediment samples were also tested during pilot tests for remediation. They were partly dehydrated and analysed on-site during pilot tests for sediment processing, including grain size separation and floatation tests (Bréquel *et al.* 2012). Dehydration was then performed by manual hand-pressing in tissue paper.

Samples collected on-site were further tested in the laboratory, both as raw wet samples and as partly dehydrated samples. This made it possible to compare field measurements on partly dehydrated samples with oven-dried samples and to quantify water losses.

For all these sample types and situations, the preparation method was the best one available at the time of the test. Most of the situations were short-lived and it was not possible to return later and test new preparation methods. This meant it was not possible to carry out a comprehensive comparison of methods, but instead reflects the continuous evolution of methods.

Analysis

pXRF parameters All pXRF measurements were performed using two Niton analysers from Thermo Scientific: the XLt999KWY and XL3t800 models. The energy dispersive XLt999KWY is equipped with a 35 kV X-ray tube (max. 35 kV, 10 µA, 1.7 W) with an Ag anode target excitation source and a Si-PIN diode detector. The analysed spot has an average diameter of 20 mm. The XL3t800 is equipped with a 50 kV X-ray tube (max. 50 kV, 100 µA, 2 W) with an Ag anode target excitation source and a Large Drift Detector (LDD). The analysed spot has an average diameter of 8 mm. As part of the standard set-up routine, the analyser was initially calibrated using silver and tungsten shielding on the inside of the shutter and the source count time for the analysis was fixed either at 30 seconds on the main filter (for quick Pb, Zn and Cu pollution identification on the canal) or at 120 seconds using the 3 filters of the pXRF unit (for a total analysis on-site or in the laboratory). All analyses were performed using the soil mode calibration provided by the manufacturer. The actual limit of detection (LOD) for Pb, Zn and Cu is matrix-dependent**.** An estimate of the LOD is evaluated by the instrument during measurements**;** it depends also upon detector performance. In a soil-type matrix, it was found to be *c.* 18, 48 and 80 mg/kg with the XLt999KWY and 8, 13 and 20 mg/kg with the XL3t800, respectively, for Pb, Zn and Cu.

Laboratory analyses Analyses were carried out by the laboratories of CTP (Tournai, Belgium) and ISSeP (Colfontaine, Belgium). In the laboratory, all samples were homogenized and then split. One sub-sample was dried at 40°C in an oven and milled (< 80 µm). Moisture was determined by weight loss in a separate sub-sample by drying at 105°C overnight. Two options for digestion were available, depending on the purpose of the analysis.

In the ISSeP laboratories, all samples were digested in aqua regia (8 ml for 0.5 g) for 45 minutes. For the analyses carried out by the CTP laboratories, a 1 g fraction was digested at 185°C in a digestion bomb with concentrated HNO_3 and HF. The samples were oven-dried at 105°C for 8 h to ensure complete evaporation of HF. Complete dryness was obtained by heating on a hot-plate up to 120°C. The dried residue was then dissolved in HNO_3 for *c.* 12 h on a hot plate at 120°C and dried again on a hotplate at 120°C. The dried residue was then dissolved again in HNO_3. In both laboratories, measurements were performed using ICP-AES.

HF digestion can be considered as near-total, while aqua regia digestion is a partial method. However, in waterway sediments, most carrier phases for the elements of interest in this paper are effectively dissolved by aqua regia.

QA/QC approach Measurements were routinely controlled using the reference material built in the instrument. Certified reference materials (CRM) such as NCS DC78301 (river sediment, China National Analysis Center for Iron and Steel, Beijing, China), RM8407 (river sediment from Oak Ridge, Tennessee, NIST) and LGC6156 (harbour sediment, Setting standards in Analytical Science) were routinely used, mainly for consistency controls.

Replicate measurements were performed during control measurements in the laboratory after the field trip. The disparity in results is smaller when repeated shots are made without moving the instrument. This suggests that matrix heterogeneity is larger than measurement variability. In this regard, the multiplication of measurements at various points on a given sample significantly improves the reproducibility of the average measurements when compared to single measurements.

The evaluation of the analytical uncertainty of each measurement is based only on the uncertainty value reported by the spectrometer for each measurement (i.e. on counting statistics). This statistical uncertainty does not include matrix heterogeneity, to be evaluated with replicate measurements on the sample.

RESULTS

Analysis of wet sludge

Raw sediments with water contents of 60 to 70% were sampled by the CTP laboratories for treatment tests. Sludge samples were measured in their raw condition by pXRF and then progressively dried in a laboratory oven. Zinc, Pb, Cu and As were the main pollutants detected by pXRF. In Figure 4, 0% refers to the raw sludge, 100% to the dried sample. Diamonds show results for various degrees of dehydration, while the error bars show the uncertainty calculated by the instrument for each measurement and the horizontal line indicates the LOD of each element.

Even if the water content of the sample is high (up to 60%), the metal content in the sample can be measured and there is a linear relationship between this value and the water content (Figure 4).

Analysis of hand-pressed sediments

During two field campaigns, samples were collected, partly dehydrated on-site by manual hand-pressing in tissue paper (Figure 2a) and then analysed on site (Figure 2b).

The water content reduction was efficient enough to improve the analytical conditions, but it was not possible to obtain the same water content in all samples. In order to determine more precisely the water content in the laboratory (Table 1), raw and pressed samples were kept in sealed bags during the second campaign.

Results by pXRF for As, Cu, Zn and Pb in wet and dried samples are shown in Figure 5, along with laboratory results by ICP-AES (aqua regia digestion). Arsenic is not reported for some samples because its content is close to or below the LOD (8 mg/kg) of pXRF. For the other elements (Cu, Zn and Pb), the first observations suggest that measured concentrations were roughly proportional to dry matter contents. Measurements on wet samples, corrected by a simple factor based on water content, are displayed together with them.

Despite large variations in measured concentrations for wet samples, the ranking of samples for each element is correctly displayed, and corrected measurements provide an acceptable approximation of the order of magnitude of the actual concentrations.

Analysis of filter-pressed sediments on-site/after drying/after drying and crushing

In order to test further the performance of pXRF on wet sediments, we tried to improve the efficiency of field dehydration. In the 2011 campaign, 85 samples were collected, dehydrated with a filter press device (Figure 3a and b) and then analysed on the boat with the XLt999KWY. Zn and Pb were the main pollutants detected by pXRF (Figure 6). Raw samples had water contents of between 35 and 58% before using the filter press device and between 24 and 38% afterwards. As for manual hand-pressing, this method enabled the water content to be reduced in all samples by between 5 and 20%. However, the range of humidity levels between samples is narrower with this method (14% instead of 33% with manual hand-pressing).

Results for Zn and Pb obtained on-site by pXRF after filter-press dehydration are compared with results obtained later, after oven drying of the field pellets (Figure 6). This is aimed at evaluating the reliability of semi-wet data vs. data obtained on properly prepared samples.

Despite a high bias on absolute measurements, the linearity of the relationship between semi-wet and dry sample data is satisfactory enough to estimate absolute concentrations on field prepared samples.

DISCUSSION

As a general rule, it is assumed here that the most suitable sample preparation procedure to maximise pXRF performance is the same as traditional laboratory analysis: drying, milling to 200 µm or less, sieving and splitting. The purpose of our study was to evaluate how far it is possible to depart from this procedure without sacrificing the representativeness of results.

How much water is acceptable in samples to rank them with respect to a given element?

Previous studies suggest that there is a roughly linear inverse relationship between water content and measured concentration. Should this relationship be really linear, it would be possible to calibrate a relationship between concentration and water content using standards and precisely measured water contents. Even a less precise relationship would nevertheless be useful, since it could enable samples to be ranked against the concentration of each element of concern.

In our results, such relationships are observed, even with values close to the LOD as for Cu, but the regression slope varies between elements. It is possible to rank samples against their Pb, Zn, Cu or As contents with water contents of between 50% and 70%.

How much water is acceptable in samples to have a rough estimate of actual concentrations?

Results from Figures 4 to 6 show that it is possible to estimate Pb, Zn, Cu or As dry concentrations from pXRF measurements on samples with water contents of between 25% and 50%, without drying them.

The same issue is faced during soil remediation projects, where decisions have to be made regarding the destination of the excavated soil. The commonly accepted rule is that pXRF measurements made on soil with water contents up to 20% (Kalnicky & Singhvi, 2001; US-EPA, 2007; Berger *et al.* 2009) or 30% (Hürkamp *et al.* 2009) are still valid.

The moisture content affects the accuracy of the analysis, mainly through sample dilution. The measured concentration decreases as the water content increases, especially for elements with low energy X-ray lines (less than 5 keV). This effect may however be counterbalanced by the reduced matrix absorption. The bias introduced by moisture is, therefore, dependent on the element and the matrix composition (Kalnicky & Singhvi 2001). Our data suggest that measurements on samples with higher water contents (30 to 50%) can still be used for decision-making, provided that they are obtained on similar matrices. Indeed, the absolute concentrations are severely affected, but in a roughly linear manner.

Correction factors were therefore calculated after measuring water contents in the laboratory (Table 1). These factors can be used to calculate corrected pXRF measurements for a given water content. Corrected measurements were found to be closer to pXRF measurements on dry samples, but also to results by ICP-AES analysis (HF digestion). The best results were obtained with Pb and Zn (Table 2 and Figure 5).

This approach to account for water content for elements such as Pb, Zn or Cu (to recalculate measurements on dry matter) has already been investigated for wet soil. For instance, a 1.51 factor was calculated by Hürkamp *et al.* (2009). However, the calculation of more precise regression coefficients shows that the correction factor is not the same for all elements (Table 2), even if it is directly correlated with the water contents.

An alternative approach to water correction would be calculating element ratios with a conservative element (for instance, Ti). This was attempted, but was not successful, due to the variation of ratios between elements of concern.

How much water is acceptable in samples to recognise elemental signatures?

In this case, despite differences between elements regarding their relation between concentration reading and water content, these differences usually do not mask the geochemical signature (Ho *et al.* 2012). Although the ranking of samples in terms of concentration remains correct, even with water contents > 50%, the slope itself varies from element to element. However, the 'signature' elemental association is little affected: a sample with predominant Cu-Zn will remain the same regardless of its concentration. Given this fact, the identification of a sediment as 'Cu-Zn rich' and another one as 'Pb-Ag rich' will be sound on the sole basis of pXRF results, even if the actual concentrations cannot be accurately given.

CONCLUSIONS

As for many other applications, pXRF provides analytical results in relation to the level of sample preparation. However, laboratory-type sample preparation is too lengthy for decision-making analyses.

There is a relationship between pXRF measurements of metal contents and the water content of the sample. This relationship can be monitored during partial or total dehydration of the sample.

The measurements of metal contents in wet samples are correlated with metal contents in dry samples, even at high moisture levels (between 30 and 70 %). No convenient method is available to measure on-site the moisture level in sediments. The most efficient way to quickly dehydrate the sample is the filter-press: it provides less variability, even if the resulting moisture level remains high.

Elements are adequately detected and samples are correctly ranked according to their contents. Element signatures are well recognised. However, the filter-press system does not dehydrate sediments enough to achieve the 20% moisture threshold. The main objective for future developments would be to obtain a more or less constant moisture level, regardless of sediment texture, composition and initial water contents (e.g. 20% +/- a few %).

The problems encountered with the water contents mainly affect the absolute accuracy of metal measurements, but they have little effect on the ranking of samples with a homogeneous composition and water content. In this regard, it is possible to build a site-specific scale of measurements with a robust relationship to the actual water contents.

Regardless of these analytical limitations, our work demonstrates that pXRF can be successfully used to evaluate the heavy metal and metalloid contamination of sediments, in a perspective of better spatial characterisation prior to dredging, of easier management during dredging works on waterways and for treatment. A proper estimation of analytical errors is required to evaluate the acceptable error risk in decision-making. This estimation is still site-dependent. Before using pXRF on wet samples for decision making, a preliminary study in laboratory conditions on similar material is still necessary.

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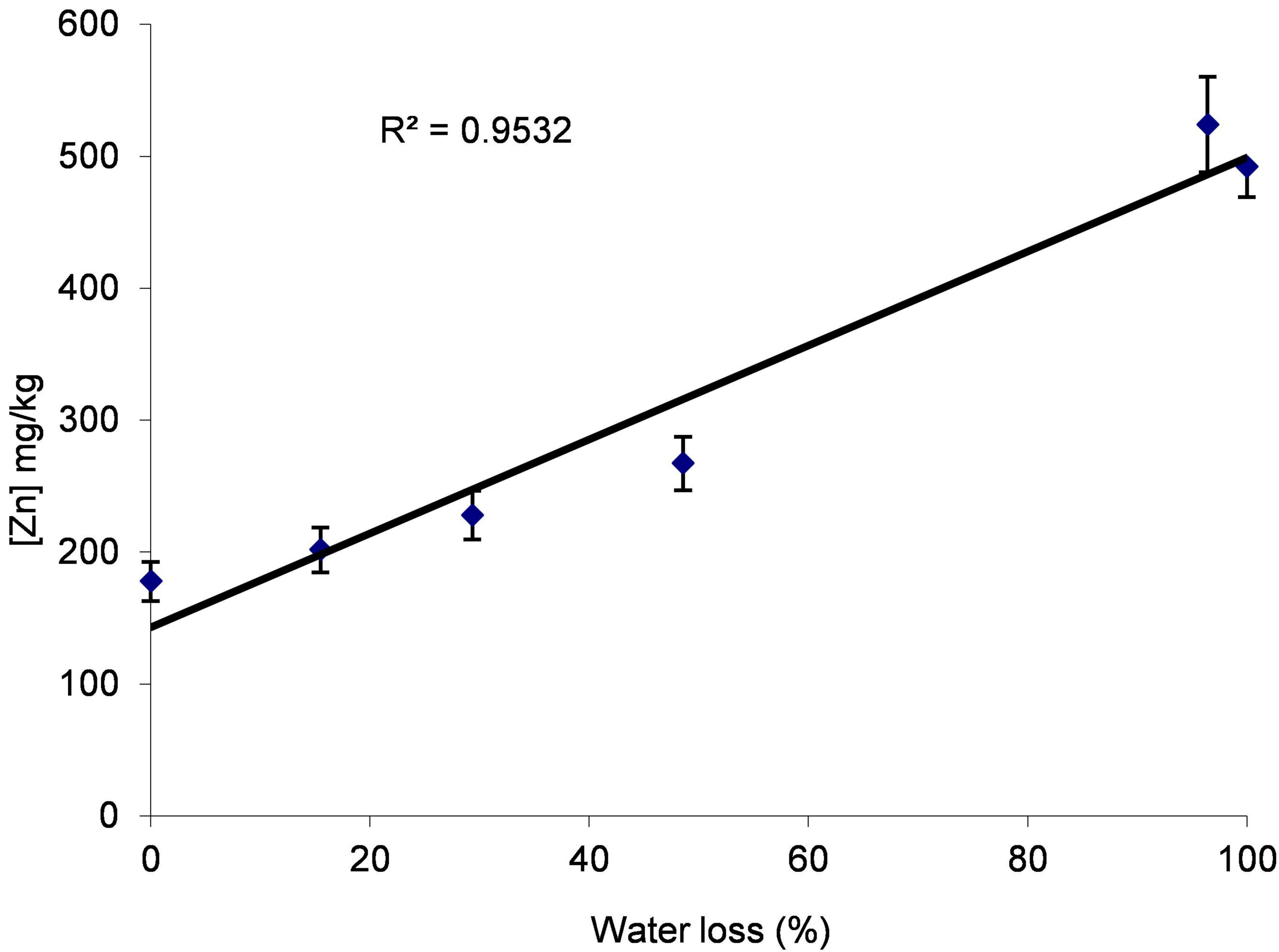
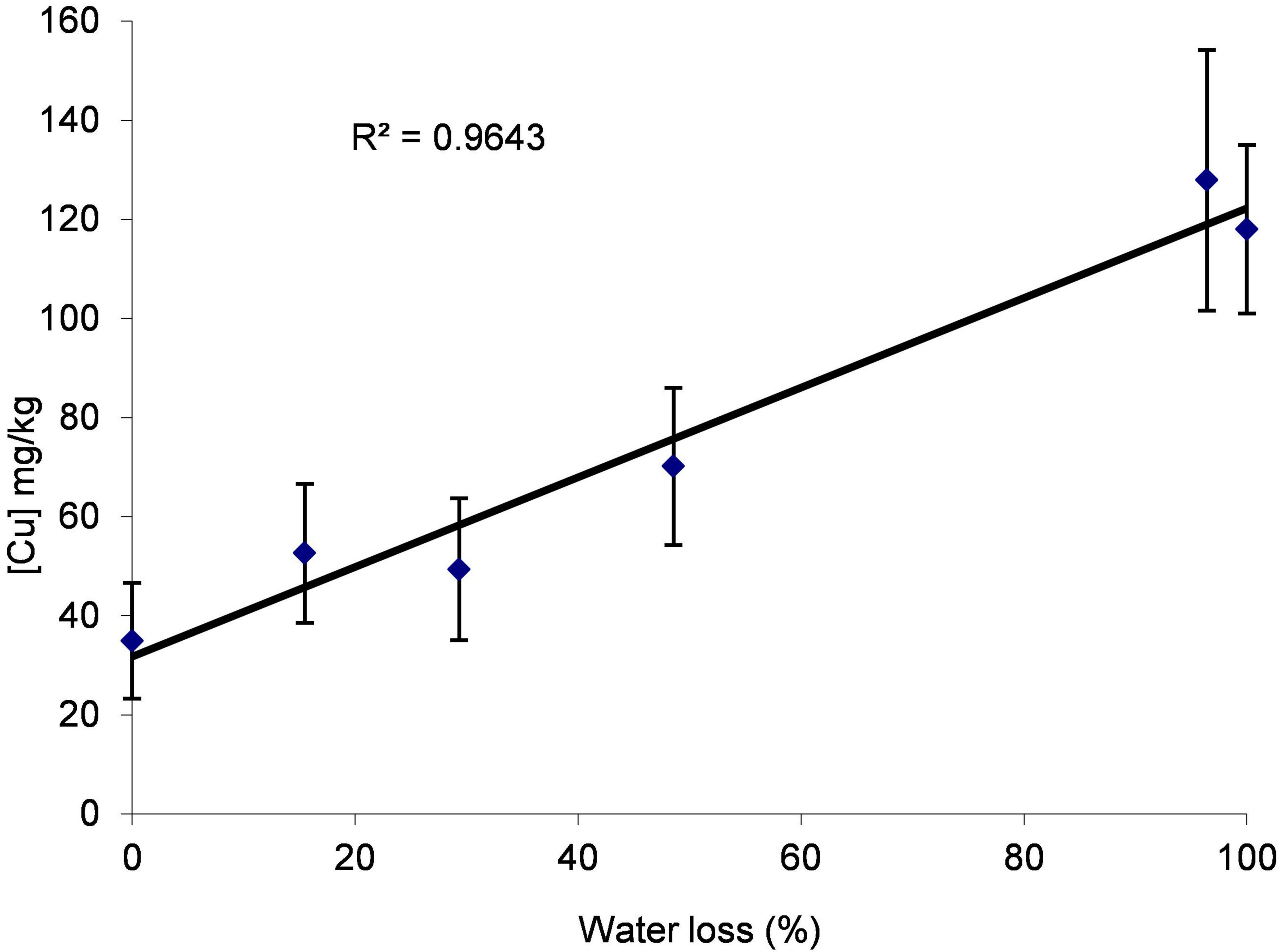
LIST OF ILLUSTRATIONS

180
150
120
90
60
30
0
[Pb] mg/kg
R² = 0.9507
0
20
40
60
80
100
Water loss (%)

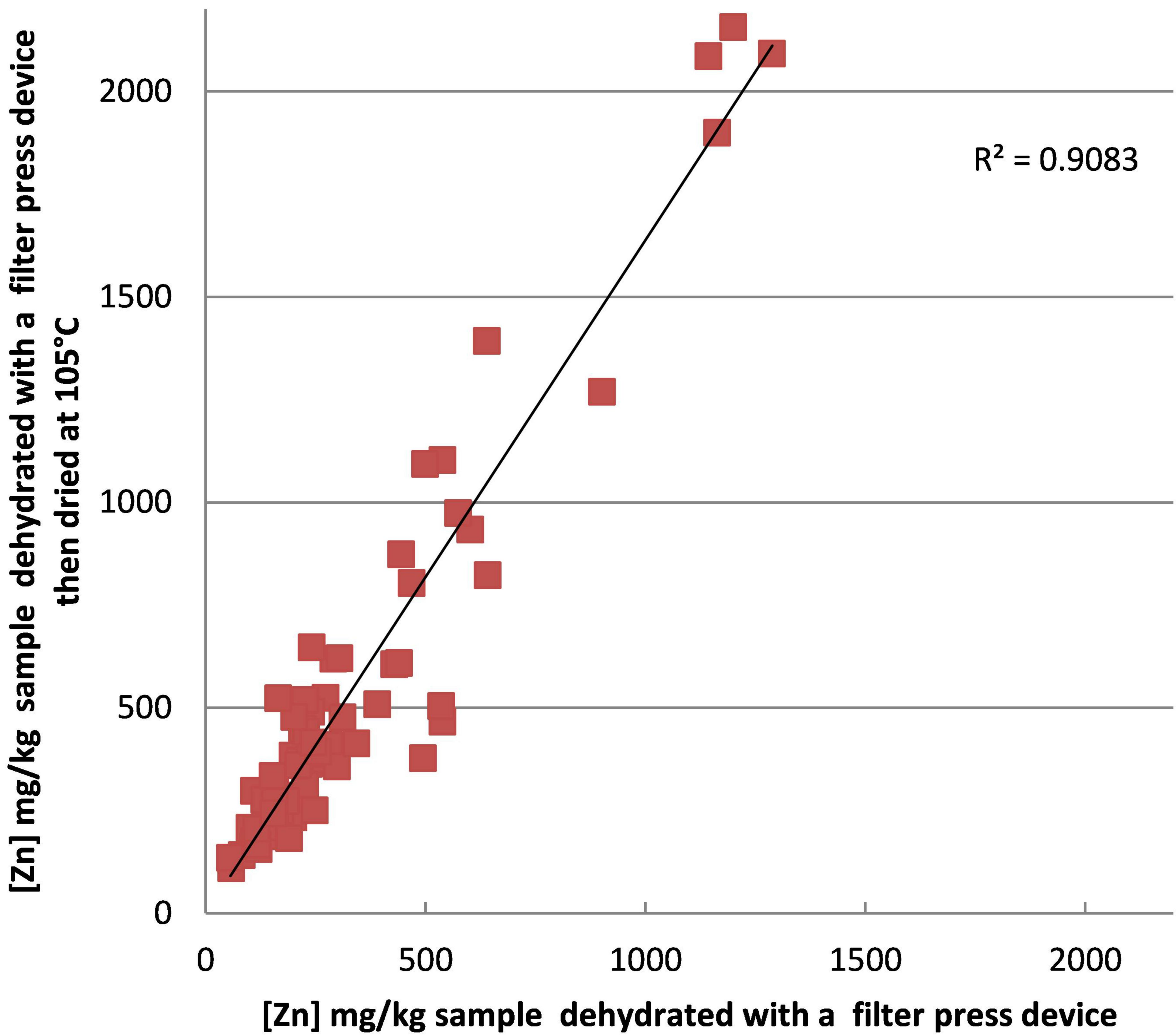


600
500
400
300
200
100
0
R² = 0.9532
[Zn] mg/kg
0
20
40
60
80
100
Water loss (%)

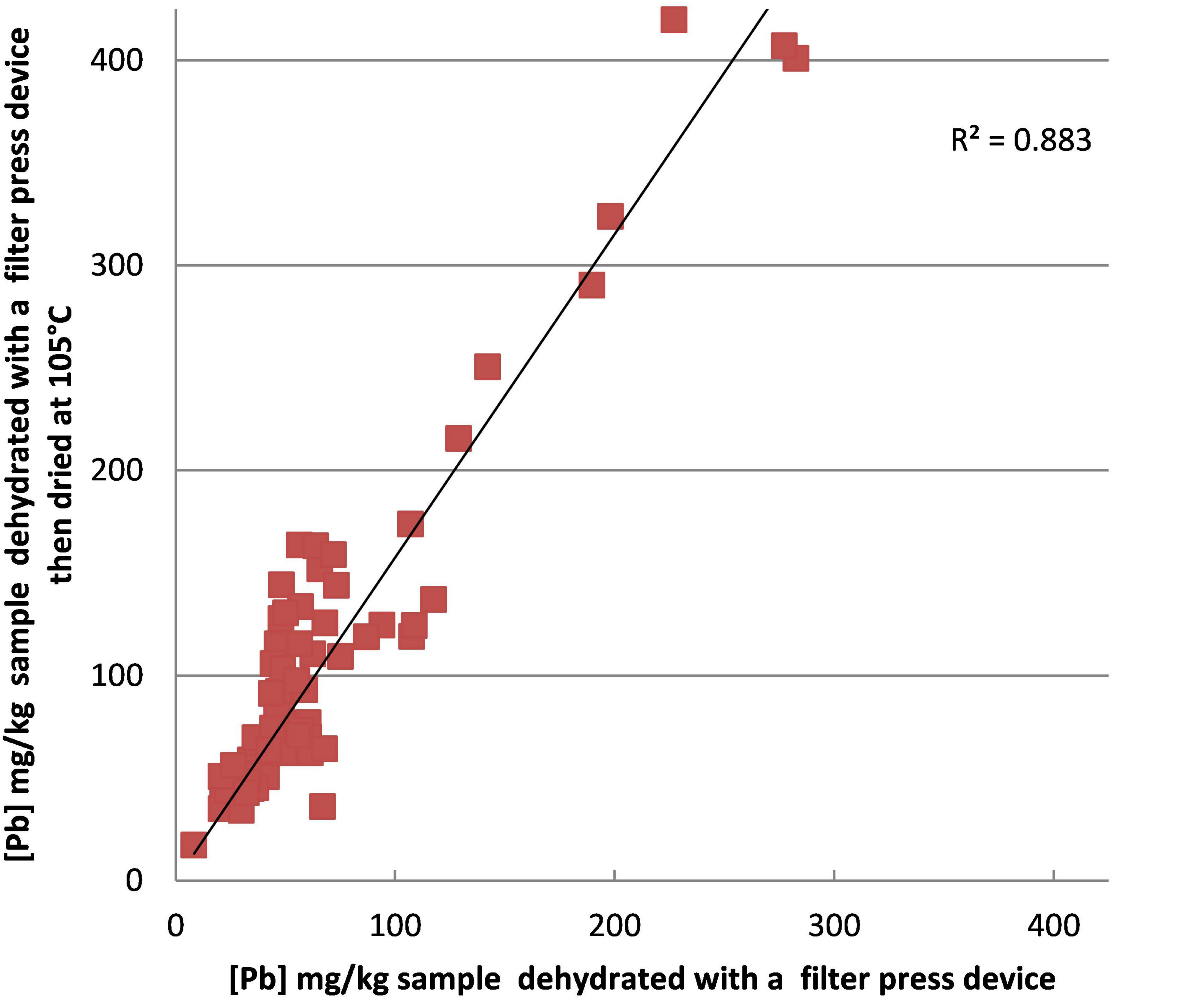


R² = 0.9643
[Cu] mg/kg
Water loss (%)
0
20
40
60
80
100
120
140
160
0
20
40
60
80
100

[As] mg/kg
[Cu] mg/kg
[Zn] mg/kg
[Pb] mg/kg
FPXRF wet
FPXRF wet corrected
FPXRF dry
ICP
CCB053
CCB054
CCB055
CCB056
CCB057
CCB058
CCB059
CCB060
CCB061
CCB062
CCB063
CCB064
CCB065



[Zn] mg/kg sample dehydrated with a filter press device
then dried at 105°C
2000
1500
1000
500
0
R² = 0.9083
0
500
1000
1500
2000
[Zn] mg/kg sample dehydrated with a filter press device



[Pb] mg/kg sample dehydrated with a filter press device then dried at 105°C
400
300
200
100
0
0
100
200
300
400
R² = 0.883
[Pb] mg/kg sample dehydrated with a filter press device

Campaign	Number of samples	Raw water contents	Water content after manual	Water content reduction
1 (sludge)	17	66.5 – 74.1%	41.6 – 52%	22 – 25%
2 (sediments)	13	40 – 65%	26 – 49%	11 – 18%

Drying time (hours)	Moisture (M) (%)	Moisture factor 100/(100-M)	[Pb] *(mg/kg)*	Corr_Pb *(mg/kg)*	Corr_Pb /ICP	[Zn] *(mg/kg)*	Corr_Zn *(mg/kg)*	Corr_Zn /ICP	[Cu] *(mg/kg)*	Corr_Cu *(mg/kg)*	Corr_Cu /ICP
Sample A	*ICP-AES*		*128*			*512*			*86*		
0	61.9	2.63	46	121	0.95	178	467	0.91	35	92	1.07
2	57.9	2.37	51	122	0.95	202	479	0.94	53	125	1.45
4	53.5	2.15	61	130	1.02	228	490	0.96	49	106	1.23
6	45.5	1.84	70	128	1.00	267	490	0.96	70	129	1.50
Sample B	*ICP-AES*		*702*			*2836*			*77*		
0	48.2	1.93	365	705	1.00	1284	2476	0.87	56	108	1.40
2	43.5	1.77	413	730	1.04	1403	2482	0.88	64	112	1.46
4	37.9	1.61	470	756	1.08	1645	2650	0.93	64	103	1.34
6	30.5	1.44	523	752	1.07	1916	2755	0.97	83	120	1.56
Sample C	*ICP-AES*		*178*			*1542*			*62*		
0	49.7	1.99	84	166	0.93	639	1269	0.82	38	76	1.23
2	36.7	1.58	114	181	1.01	864	1365	0.89	64	100	1.62
4	28.4	1.40	129	180	1.01	966	1348	0.87	76	106	1.70
6	18.0	1.22	152	186	1.04	1172	1430	0.93	82	100	1.61
8	8.2	1.09	188	205	1.15	1312	1429	0.93	121	132	2.13
10	4.3	1.04	191	200	1.12	1381	1442	0.94	106	111	1.79