

The efficiency of acid/peroxide digestion followed by ICP-MS on varying soil-biosolids mixtures versus WD-XRF Spectrometry

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Abstract

The application of biosolids to agricultural land can provide macro and micro nutrients, and organic matter; however, the accumulation of metals in soils amended with biosolids is a potential concern. Hence there is a need for a robust and accurate analytical technique for measuring metals in both biosolids and biosolids-amended soil. Here we compare two analytical techniques, Wavelength Dispersive- X-ray Fluorescence Spectrometry (WD-XRF) and acid/peroxide digestion followed by Inductively Coupled Plasma-Mass spectrometry (ICP-MS). A field experiment was conducted using varying applications of two types of biosolids on a clay loam soil. At the end of first harvest, biosolids-amended soils were analyzed for “total” metals (Cu, Zn, Fe, Mn, Pb) using the two analytical techniques. The metal concentrations in the residual soils as determined by WD-XRF were significantly higher than their corresponding ICP-MS (HNO₃/H₂O₂ extracted) values. However, an increase was observed in the ICP-MS: WD-XRF metal concentration ratio at higher application rates of biosolids, demonstrating that extraction with HNO₃/H₂O₂ is better where the metals are associated with organic matter. While it is well known that there is a pool of metals not readily accessible through acid digestion, the change in extraction efficiency with increasing applications of organic matter is often overlooked. Better reproducibility and recovery was obtained in the analysis of heavy metals in standard reference materials using WD-XRF. The results obtained from WD-XRF were close to the calculated expected values and therefore is recommended for routine laboratory analysis of soils amended with biosolids when an estimate of the total metal concentration is required.

Keywords: HNO₃/H₂O₂ extractable; ICP-MS; WD-XRF, Total metals; Biosolids-amended soil

31 **1. Introduction**

32 There is increasing interest in the land application of biosolids for agricultural purposes due to
33 their nutrient and organic matter content, and increasing price of fertilizers. However, biosolids
34 often contain significant quantities of metals as a result of industrial inputs, particularly where
35 the domestic waste stream is not segregated from the industrial waste stream, as in Victoria,
36 Australia. This can lead to a build-up of metals in the receiving soil over a period of time which
37 needs to be monitored, since there is potential for crop uptake.

38 One of the recommended procedures for the analysis of metals in plants and in soils amended
39 with biosolids is extraction by $\text{HNO}_3/\text{H}_2\text{O}_2$ followed by ICP-AES [1]. ICP-MS can also be used [2].
40 The most common types of environmental samples analysed by ICP-MS include drinking waters,
41 ground waters, wastewaters, river waters, estuarine waters, seawaters, solid waste, soils,
42 sludges, sediments, and airborne particulates [3]. The analysis time is rapid, allowing replicate
43 analyses, external and internal standardization and quality control procedures in line with the
44 U.S. Environmental Protection Agency's guidelines [4]. However, the preceding extraction
45 process is time consuming and potentially hazardous, particularly when using perchlorate
46 and/or hydrofluoric acid in the digestion process.

47 By comparison, Wavelength Dispersion X-ray Fluorescence Spectrometry (WD-XRF) is the most
48 widely used technique for the routine analysis of geological samples such as rocks, soils and
49 sediments where major and common trace element data are required [5, 6]. Furthermore, it is a
50 non-destructive analytical technique [7]. The advantages of using WD- XRF for elemental
51 analysis include: fast analysis time, low cost per sample and good accuracy and precision [8].
52 Sample preparation is minimal compared to conventional analytical techniques as it avoids acid
53 digestion with concomitant dilution of the samples. The sample measurement time is in the
54 order of a few minutes and automatic sample changing is possible. Hence WD-XRF may be
55 viewed as an equivalent alternative technique to ICP-MS for the analysis of soils and soils
56 amended with biosolids.

57 The relationship between WD-XRF and a number of other techniques has been explored
58 previously. For instance, Wilson et al. analysed potentially contaminated soils for Cu and Zn
59 contents using ICP-OES and WD-XRF techniques and suggested that results obtained by WD-XRF
60 were slightly higher than those obtained by ICP-OES, due to incomplete digestion of the samples
61 in preparation for analysis by ICP-OES [9]. Mäkinen et al. analysed Cu, Cr and As in soils polluted
62 by chromated copper arsenate using WD-XRF and FAAS [10]. Their findings showed a good
63 correlation for As and Cu between the two methods.

64 Duane et al. analysed heavy metals in soil samples collected from a disused industrial area in
65 order to evaluate the performance of a mobile laboratory equipped with ICP-MS (aqua regia

66 digested) and compared the results with fixed-lab based ICP-AES/GFAAS and ED-XRF [11]. From
67 the analysis of CRM-320 reference material, it was reported that except for Cr, Zn and Pb, WD-
68 XRF and ICP-MS produced similar results

69 More recently, Palmer et al [12] compared the efficiency of Field-Portable XRF Analyzers with
70 laboratory based ICP-MS to screen toxic elements, and concluded that the Field-Portable XRF
71 instrument is a remarkably valuable tool for routine and non-routine elemental examinations,
72 both in the laboratory and in the field.

73 In this paper we compare the concentrations of “total” metal residuals in soils amended with
74 biosolids as determined using ICP-MS and WD-XRF. The samples for “total” metal analysis by
75 ICP-MS were extracted using a solution of concentrated nitric acid (70 %) and hydrogen
76 peroxide (30 %).

77 The reproducibility and accuracy of the two analytical techniques are compared, and the
78 influence of biosolid type on the response measured.

79 **2. Materials and Methods**

80 *2.1. Experimental Set up and Biosolid Treatments*

81 Anaerobically digested dewatered biosolids were supplied from the Western Water Recycled
82 Water Plant at Surbiton Park(WWSP), Melton, Victoria Australia and composted biosolids were
83 supplied from Pinegro (a compost supplier); the biosolids composting firm sources its biosolids
84 from the Western Water recycled water treatment centre at Sunbury, Victoria and combines
85 them with vegetable waste. The biosolids produced at the two treatment plants come from
86 similar sources and undergo equivalent processing.

87 An experimental site was reserved for conducting the biosolids field trial at WWSP. The site had
88 no cropping or any history of fertiliser application (or application of biosolids). Samples of soil
89 and biosolids were taken before sowing the crop to determine their initial physicochemical
90 properties.

91 The land was partitioned into 36 x 12 m² experimental plots {(2 biosolids x 5 application rates) +
92 2 x fertiliser controls} x 3 replicates} and canola (*Brassica napus*, cultivar Beacon) was used as
93 the trial crop [13]. Control plots using conventional fertilizers were established using urea (46%
94 nitrogen) at a rate of 100 kg/ha. Two experiments, one with the anaerobically dewatered
95 biosolids and the other with composted biosolids, were performed in triplicate in a randomized
96 complete blocked design. Canola seeds were sown at a seeding rate of 5 kg/ha. Biosolids were
97 added at a rate of 0, 5, 25, 45 and 65 t dry solids(ds)/ha for dewatered biosolids and 0, 10, 30,

98 50 and 70 t ds /ha for composted biosolids respectively, and incorporated into the top 10 cm of
99 the soil.

100 *2.2 Soil and Biosolids Sampling and Analysis*

101 Before establishing the field experiment at WWSP, composite top soil samples from the
102 experimental site and dewatered biosolids and composted biosolids were sampled, air dried for
103 two weeks, sieved through a 2 mm mesh and analysed for metals using ICP-MS and WD-XRF.

104 An Eijkelkamp sample ring kit, model 07.53 SC (Eijkelkamp Earth Sampling Group 'Royal'), was
105 used for the measurement of soil bulk density. The cylinder (of known dimensions) was
106 hammered into the soil and carefully removed to collect the entire soil sample. Five fresh soil
107 samples were taken from each of the experimental sites. The samples were dried to a constant
108 mass at 105°C to obtain the dry weight. The soil bulk density was calculated from the total dry
109 mass of the sample (g) divided by the volume of cylinder (cm³).

110 The moisture content of soil and biosolids samples was determined according to Method 2A1 of
111 Rayment and Higginson [14]. The pH_w, pH_{Ca} and EC of soil and biosolids were determined as
112 per Methods 4A1, 4B2 and 3A1 of Rayment and Higginson [14], respectively. Total nitrogen and
113 carbon were determined using a Leco FP 2000 Carbon and Nitrogen Autoanalyzer at the State
114 Chemistry Laboratory (Werribee, Victoria). The major cations were determined by Method 15A1
115 of Rayment and Higginson [14] and iron and potassium were measured using WD-XRF [13].

116 Samples of soils amended with biosolids were analysed for total metals from each of the
117 treatment plots after six months (following crop harvest)

118 *2.3. Metal analysis*

119 *2.3.1. ICP-MS analysis*

120 The concentrations of metals in soil and biosolids were determined according to the procedures
121 described by Jones[15] by weighing 0.5 g samples into 5 mL of 70% nitric acid in 150 mL Pyrex
122 tubes and pre-digesting at room temperature for 30 min. Samples were digested in an
123 aluminium block at 125°C for 1 hr and then 3 mL of 30% hydrogen peroxide was added to each
124 tube. After 1 hr of digestion, the Pyrex tubes were removed from the digestion block and
125 allowed to cool. An additional 2 mL aliquot of 30% hydrogen peroxide was added to each of the
126 samples and digested at 125°C for a further 2 hr.

127 After a total digestion time of 4 hr, samples were removed from the digestion block and allowed
128 to cool to room temperature. The digest was filtered (Whatman No. 42) and quantitatively
129 transferred to 50 mL volumetric flasks using 2% nitric acid.

130 For the analysis, 0.5 mL of the extract was added to a 50 mL volumetric flask and diluted with 2
131 % nitric acid. Calibration standards were prepared from a multi-element stock analytical grade
132 environmental calibration standards solution (100 ppm for major cations and 10 ppm for trace
133 elements: Agilent Technology Worldwide Environmental USA calibration solutions part number
134 5183-4688). Samples, standards and blanks were spiked with 0.5 mL (5000 ppb) praseodymium
135 as an internal standard to check for matrix effects and instrument drift. Samples, standards and
136 blanks were all diluted using 2 % nitric acid and the metals (Cu, Zn, Mn and Fe) were determined
137 using an Agilent Technologies Model 4500 series 300 ICP-MS with HP ChemStation software
138 with detection limits for the Quadrupole of 1-10 ng/L and for the magnetic sector of 0.01- 0.1
139 ng/L.

140 *2.3.2. X-ray fluorescence (WD-XRF) analysis*

141 Total metals in soil, biosolids and biosolids-amended soil samples were analysed using a Bruker
142 S4 Pioneer (Bruker AXS, Karlsruhe, West Germany) Wavelength Dispersive- X-Ray Fluorescence
143 Spectrometer, equipped with LiF (200), Ge, PET, ovo-55 crystals with detection limits ranging
144 between 10-100 µg/g for soil (Schlotz and Uhlig, 2002).

145 X-ray fluorescence analysis was carried out by weighing 8 g of soil/biosolids or biosolids-
146 amended soil samples and adding 2 x 0.5 g wax based briquetting tablets (PXR-250 Choice
147 Analytical, Thornleigh, NSW). The samples were ground using a Zirconia Ring Mill (Rocklabs,
148 Auckland, New Zealand). The fine particulate samples were transferred into 40 mm aluminium
149 cups and pressed at 10 tonnes. The pressed pellets were analysed in triplicate.

150 *2.4. Statistical Analysis*

151 The analytical data were subjected to analysis of variance (ANOVA) F-tests for each experiment
152 using Genstat Release 9 [16]. Differences between means were compared by the Fisher's least
153 significant difference (LSD) t-test using a significance of $P < 0.05$.

154 **3. Results and Discussions**

155 *3.1. Physicochemical Properties of Soil and Biosolids*

156 Selected physicochemical properties of the soil and two biosolids are shown in Table 1 below.
157 The pH and dry matter content of soil and biosolids were similar; however, the biosolids had
158 higher total and extractable concentrations of both macro and micro nutrients.

159

160 Table 1 Physicochemical properties of soil and biosolids

Analytes	Soil	Dewatered biosolids	Composted biosolids
pH _w	6.5	6.7	6.4
Moisture (%)	2	8	11
pHCaCl ₂	5.5	6.2	6.1
EC (1:5)(μ S/cm)	67.4	1350	2704
CEC (meq/kg)	6.9	24	62
Total N %	0.17 \pm 0.002	4.22 \pm 0.01	1.44 \pm 0.003
Total C %	2.04 \pm 0.02	31.0 \pm 0.1	13.85 \pm 0.04
C/N	12.2	7.4	9.6
Total P (μ g/g)	855 \pm 3	15003 \pm 4	21290 \pm 566
Total S (μ g/g)	239 \pm 1	11380 \pm 1	5265 \pm 6
Total K (%)	1.071 \pm 0.005	0.389 \pm 0.001	1.240 \pm 0.002
Total Fe (%)	2.78 \pm 0.05	1.36 \pm 0.01	2.5 \pm 0.1
Total P, S, Fe and K were determined using WD-XRF (n = 3). All analytical results are expressed on air dry basis			

161

162 *3.2. Validation of analytical data*

163 *3.2.1 ICP-MS analysis*

164 To ensure quality control for the data generated from ICP-MS, the certified reference material
 165 CRM 031-040 (sewage sludge) was analysed in duplicate after every 18 samples of biosolids-
 166 amended soil. Table 2 shows the results obtained for Cu, Zn, Mn and Fe along with their
 167 certified reference values. The recoveries were all within the certified values.

Table 2 Recoveries of 'total' metals in CRM031-040 digested with HNO₃ /H₂O₂ and analyzed by ICP-MS (expressed in μ g/g)

Elements	Measured	Certified	Recovery (%)
Cu	730 \pm 20	805 \pm 91.1	88-90
Zn	1300 \pm 100	1060 \pm 88.6	88-119
Mn	190 \pm 60	199 \pm 24.6	89-96
Fe	9300 \pm 100	9810 \pm 824	88-94

The CRM031-040 (Sewage sludge standard reference material) was analyzed using ICP-MS in duplicate and values indicate mean \pm sd for each of the elements

168

3.2.2. *WD-XRF analysis*

169 For the WD-XRF analysis of total metals in soil, biosolids and biosolids-amended soils, calibration
170 curves for each of the metals were established using eight soil standard reference materials
171 (NCS DC 73319, NCS DC 73320, NCS DC 73321, NCS DC 73322, NCS DC 73323, NCS DC 73324,
172 NCS DC 73325 and NCS DC 73326, China National Analysis Centre for Soil and Steel, Beijing,
173 China). Table 3 shows the measured and certified values of these standard reference materials.

174 To validate the established calibration curves, other soil standard reference materials (Till-1 and
175 Till-3, Canada Centre for Mineral and Energy Technology, Ottawa, Canada) were treated as
176 samples and analysed for Cu, Zn, Mn and Fe. The percentage recoveries of each of the metals
177 are shown in Table 4. The percentage recovery ranged between 93-108 for Cu, 97-117 for Zn,
178 92-104 for Mn and 96-102 for Fe.

Table 3 Total metal concentrations of eight soil standard reference materials with their percentage recovery analysed using WD-XRF (expressed in $\mu\text{g/g}$)

Soil SRM	Cu	Zn	Mn	Fe
NCS 73319 Certified	21 \pm 2	680 \pm 25	1760 \pm 63	51900 \pm 900
Measured	20	679	1730	52000
Recovery (%)	95	100	98	100
NCS 73320 Certified	16.3 \pm 0.9	42 \pm 3	510 \pm 16	35200 \pm 700
Measured	18	49	470	34000
Recovery (%)	110	117	92	97
NCS 73321 Certified	11.4 \pm 1.1	31 \pm 3	304 \pm 14	20000 \pm 500
Measured	12	33.7	290	20000
Recovery (%)	105	109	95	100
NCS 73322 Certified	40 \pm 3	210 \pm 13	1420 \pm 75	103000 \pm 1100
Measured	40	214	1400	104000
Recovery (%)	100	102	99	101
NCS 73323 Certified	144 \pm 6	494 \pm 25	1360 \pm 71	126200 \pm 1800
Measured	141	490	1340	127000
Recovery (%)	98	99	99	101
NCS 73324 Certified	390 \pm 14	97 \pm 6	1450 \pm 82	80900 \pm 1300
Measured	390	94	1500	83000
Recovery (%)	100	97	103	103
NCS 73325 Certified	97 \pm 6	142 \pm 11	1780 \pm 113	187600 \pm 3300
Measured	100	151	1820	187000
Recovery (%)	103	106	102	100
NCS 73326 Certified	24.3 \pm 1.2	68 \pm 4	650 \pm 23	44800 \pm 500
Measured	24	70	600	44000
Recovery (%)	99	103	92	98

Note: Data behind “ \pm ” indicates uncertainty, $U = t\alpha \times S/\sqrt{N}$, where $\alpha = 0.01$, S refers to standard deviations and N for number of data ($N > 8$). For the measured values the standard deviations of the calibrated metals were: Cu (± 4); Zn (± 5); Mn (± 10), Pb (± 3) and Fe (± 0.6).

Table 4 Total metal concentrations of soil Standard Reference Materials Till-1 and Till-3 analyzed by WD-XRF (expressed in $\mu\text{g/g}$)

Till1	Measured	Certified	Recovery%	Till3	Measured	Certified	Recovery %
Cu	44	47	93	Cu	20	22	93
Zn	90	98	91	Zn	54	56	97
Mn	1310	1420	92	Mn	451	520	87
Fe	43500	48100	91	Fe	25000	27800	93

180

181 *3.3. Total metal concentrations in soil and biosolids*

182 Table 5 below shows the concentrations of metals in soil and biosolids determined by ICP-MS.

Table 5 ‘Total’ metals in soil, dewatered biosolids and composted biosolids determined by ICP-MS (expressed in $\mu\text{g/g}$) n=3

Analytes	Soil	Dewatered biosolids	Composted biosolids
Cu	9 ± 1	416.0 ± 0.1	138 ± 1
Zn	2.0 ± 0.3	519 ± 1	365 ± 45
Mn	134 ± 2	170 ± 26	319 ± 4
Fe	25900 ± 350	9400 ± 150	28600 ± 150

183

184 Table 6 below shows the results from the analysis on the same samples using WD-XRF, which
 185 are all clearly higher.

Table 6 WD-XRF determined concentrations of total heavy metals in soil, dewatered biosolids and composted biosolids (expressed in $\mu\text{g/g}$) n=3

Analytes	Soil	Dewatered biosolids	Composted biosolids
Cu	17.0 \pm 0.8	648 \pm 1	210 \pm 4
Zn	37 \pm 2	1062 \pm 1	813 \pm 8
Mn	246 \pm 2	213 \pm 1	299 \pm 6
Fe	26000 \pm 1000	14000 \pm 100	25000 \pm 1000

Values indicate mean \pm standard deviations of triplicate measurements

186 In both sets of analyses, the concentrations of Cu and Zn in dewatered biosolids were higher
 187 than the levels found in composted biosolids, whereas Fe was higher in composted biosolids.
 188 The concentrations of most of the metals found in the soil were significantly lower than the
 189 levels found in both biosolid types with the exception of Fe and Mn.

190 The higher levels of Mn observed in the composted biosolids could be due to composting
 191 processes which increases the relative concentration of heavy metals due to the microbial
 192 degradation of the organic matter and loss of volatile solids.

193 *3.4. Biosolids application and metals loading rates*

194 Based on the concentration of metals in the biosolids (from Table 6), the expected final
 195 concentration of metals applied to the soil was calculated using a soil bulk density of 1.51 g cm^{-3}
 196 and a biosolids incorporation depth of 10 cm. The data are shown in Table 7. (The background
 197 concentration of the soil has been taken into account.)

198

Table 7 Dewatered biosolids (DW) and composted biosolids(CB) application rates and their corresponding expected metal concentrations in the soil after application ($\mu\text{g metal/g biosolids-amended soil}$)

DWB rates (t/ha)	Cu	Zn	Mn	Fe
5	17	34	195	27800
25	26	49	197	28000
45	34	63	200	28200
65	43	77	203	28400
CB rates (t/ha)	Cu	Zn	Mn	Fe
10	16	36	196	27900
30	19	47	200	28200
50	22	58	204	28600
70	25	69	208	28900
DL WD-XRF	3	3	6	500
DL ICP-MS	0.7	2.2	1	7

200

201 These calculations suggest that the predicted changes should be observable for Cu and Zn but
 202 only marginally for Fe or Mn. This is observed in Figures 1 and 2.

203

204

205

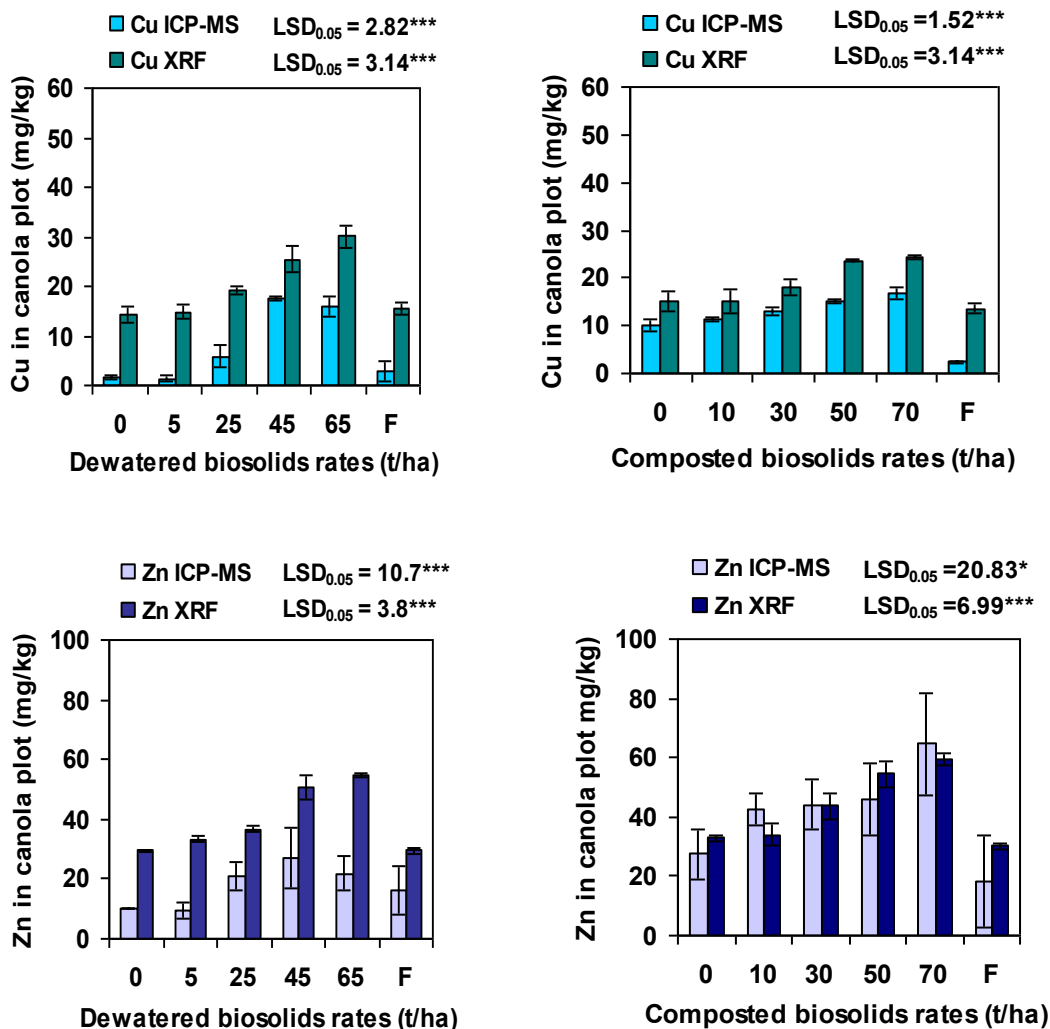


Figure 1 A comparison between ICP-MS and WD-XRF determined total Cu and Zn in dewatered biosolids and composted biosolids amended soils sampled from canola plots. LSD 0.05 refers to the least significant difference (t-test) between the mean values at the 5 % probability level. The error bars indicate standard deviations of triplicate measurements, whereas, *** refers to significant treatments effects in ANOVA (F-test) at $p < 0.001$ level.

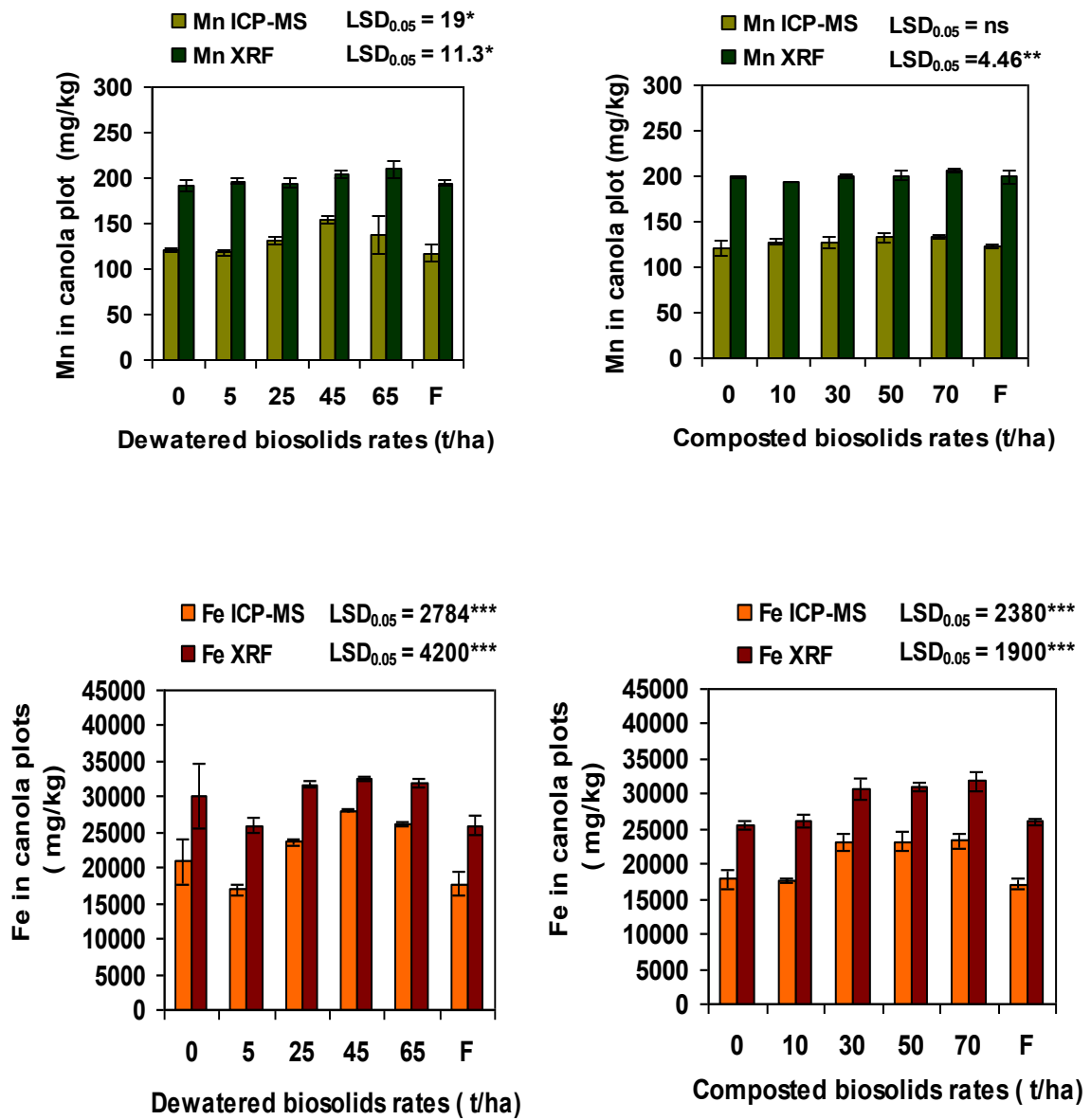


Figure 2 A comparison between ICP-MS and WD-XRF determined total Mn and Fe in dewatered and composted biosolids amended soils sampled from canola. LSD 0.05 refers to the least significant difference (t-test) between the mean values at the 5 % probability level. The error bars indicate standard deviations of triplicate measurements, whereas, *, ** and ns refers to significant treatments effects in ANOVA (F-test) at $p < 0.05$, $p < 0.01$ and not

significant respectively

206 Figure 1 shows the change in residual “total” Cu and Zn as measured by WD-XRF and ICPMS, at
207 each application rate, for each type of biosolid. When the results of the two techniques are
208 compared, a number of observations can be made.

209 Both methods showed more of an increase in the Cu in the plots treated with dewatered
210 biosolids than in the plots treated with composted biosolids. This is consistent with the Cu
211 concentration in the dewatered biosolids being almost 4 times greater than the composted
212 biosolids.

213 On average, Cu results recorded from WD-XRF analysis were 47% more in dewatered biosolids
214 treated plots and 50 % more in the composted biosolids treated plots than those measured
215 using ICP-MS.

216 Concentrations of Zn recorded from WD-XRF analysis were also significantly higher than the Zn
217 levels recorded from ICP-MS analysis. WD-XRF on average gives 53% more Zn in dewatered
218 biosolids treated plots than the corresponding Zn values recorded from the ICP-MS technique.

219 In the composted biosolids treated plots, the residuals of Zn determined using WD-XRF and ICP-
220 MS were similar. Using either technique, it can be seen that concentrations of Zn residues in
221 biosolids amended soil significantly increased following increased dewatered biosolids and
222 composted biosolids application rates (Figure 1).

223 Figure 2 shows the results for Mn and Fe. While it was not expected that any significant
224 increase would be evident, the relationship between the results for WD-XRF and ICP-MS can be
225 clearly seen. For plots treated with dewatered biosolids, the Mn results from WD-XRF were on
226 average 34% higher than the corresponding results obtained from ICP-MS; for plots treated with
227 composted biosolids this difference was 41% (Fig 2).

228 Concentrations of Fe determined by WD-XRF in the dewatered biosolids amended plots were
229 higher than the levels observed in ICP-MS analysis by 27%; likewise the Fe concentration
230 determined by WD-XRF was 36% higher than the ICP-MS results in composted biosolids-treated
231 plots.

232 These results follow the same pattern as those from Chander et al. [17], who compared the
233 relationship between aqua regia, HNO₃ pressure digested (ICP-AES) and WD-XRF determined
234 heavy metals in contaminated soil. They reported that the aqua regia digestible fraction of Cu
235 and Zn reached on average 64% of the WD-XRF-detectable content, whereas the pressure
236 accelerated HNO₃-digestible fraction of the metals was on average 71% of the WD-XRF-
237 detectable content.

238 The values from WD-XRF closely match those predicted in Table 7. However, these calculations
239 are based on a 10 cm incorporation depth, which in practice is difficult to ensure. Therefore, a
240 1:1 correspondence was not expected.

241 *3.5. Relative extractability of metals in biosolids amended soil*

242 The relative extractability ($\text{HNO}_3/\text{H}_2\text{O}_2$) of the 'total' metals determined using ICP-MS expressed
243 as percent of WD-XRF total for biosolids amended soils is shown in Table 8. For comparison
244 purposes, the ratio of ICP-MS to WD-XRF total metal concentrations for the dewatered and
245 composted biosolids are also presented.

246 The data for the ratio of ICP-MS to WD-XRF determined total metals for Cu, Zn, Mn and Fe show
247 some variation following dewatered biosolids application rates. There is an increase in the ratio
248 of ICP-MS to WD-XRF percent values with increasing dewatered biosolids application rates,
249 which is pronounced for Cu. Likewise, there is a slight increase in the ratio of ICP-MS to WD-XRF
250 percent values for Cu, Zn, Mn and Fe with increasing composted biosolids application rates
251 (Table 8).

252 The small but significant increase in the ratio of ICP-MS to WD-XRF percent values for Cu
253 following dewatered biosolids application rates is likely to be due to the association of Cu with
254 increased organic matter added to the soil from the biosolids. Similarly, it was observed that the
255 ratio was greater for Mn from the biosolids alone. Since, the amount of Mn in the biosolids was
256 low compared to the receiving soil, it is not surprising that no change in the ratio was observed
257 with increasing application rate.

258 From these results, it is clear that digestion with $\text{HNO}_3/\text{H}_2\text{O}_2$ was more effective on samples
259 with high organic matter content for Cu and Mn, contributing to increases in the values for the
260 ratio of ICP-MS to WD-XRF determined heavy metals values at various biosolid application rates.
261 However, it is also apparent that the ratios are different for different metals and different for
262 different types of biosolids.

263 The values obtained from WD-XRF were close to the predicted values. Since WD-XRF analysis
264 does not depend upon biosolid type, is fast and reproducible.

265

Table 8 Comparison between WD-XRF total and ICP-MS (HNO₃/H₂O₂ extracted) total metals in dewatered biosolids and composted biosolids amended soils (ICP-MS values expressed as percent of WD-XRF total).

Dewatered biosolids treated soil				
Dewatered biosolids rates	Cu	Zn	Mn	Fe
	%	%		
	ICP/ XRF	ICP/XRF	% ICP/XRF	% ICP/XRF
0	12	34	63	70
5	9	28	60	66
25	30	57	68	74
45	68	54	76	86
65	53	40	66	82
Dewatered biosolids	64	49	80	67
Composted biosolids treated soil				
Composted biosolids rates	Cu	Zn	Mn	Fe
	% ICP/ XRF	% ICP/XRF	% ICP/XRF	% ICP/XRF
0	67	84	61	70
10	76	125	66	68
30	71	101	64	76
50	64	84	66	75
70	69	109	65	73
Composted biosolids	66	45	107	114

268

269 **4 Conclusion**

270 Levels of Cu, Zn and Fe determined using both ICP-MS and WD-XRF in biosolids amended soil
271 increased as both types of biosolids application rates increased, with total metals determined
272 by WD-XRF being significantly higher than their corresponding values determined by ICP-MS.

273 Slight increments in the values of the ratio of ICP-MS to WD-XRF values for Cu at higher biosolids
274 application rates (45 and 65 t/ha dewatered and 50 and 70 t/ha composted biosolids treated
275 soils) was noted, suggesting that HNO₃/H₂O₂ extractable fractions of the metals were partly
276 affected by the organic matter content of the amended soil.

277 WD-XRF is a better option for total metal analysis particularly for soil analysis due to its shorter
278 time of sample preparation and ease of instrument operation. Since there is no pre-
279 concentration step, this saves time and avoids the risks from contamination. Furthermore,
280 chemical reagents are not required, significantly reducing analytical costs.

281 In addition to this, better reproducibility as achieved with WD-XRF and can therefore we
282 recommend its use for biosolids and soils amended with biosolids when total metal analysis is
283 required.

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