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Novel use of field-portable-XRF for the direct analysis of trace elements in marine macroalgae

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Abstract

Samples of dried marine macroalgae (*Fucus serratus*, *Palmaria palmata* and *Ulva lactuca*) have been analysed for trace elements by a novel, non-destructive approach involving a Niton field-portable-x-ray fluorescence (FP-XRF) spectrometer configured in a low density plastics mode with thickness correction. Detection limits for a 200-second counting time ranged from < 5 μg g^{-1} for As and Pb in *F. serratus* and As in *P. palmata* to several tens of μg g^{-1} for Cd, Sb and Sn in all species tested. Arsenic, Cu, Pb and Zn were detected by the XRF in samples collected from a protected beach (n = 18) and in samples therefrom that had been exposed to additional aqueous elements in combination (n = 72) with concentrations returned (in μg g^{-1}) ranging from 3.9 to 39.7 for As, 13.0 to 307 for Cu, 6.1 to 14.7 for Pb and 12.5 to 522 for Zn. Independent measurements of trace elements in the macroalgae by ICP-MS following nitric acid digestion revealed a direct and significant proportionality with concentrations returned by the XRF, with slopes of the XRF-ICP relationships (As = 1.0; Cu = 2.3; Pb = 2.4; Zn = 1.7) that can be used to calibrate the instrument for direct measurements. The approach shows potential for the in situ monitoring of macroalgae in coastal regions that is currently being investigated.

Keywords: marine macroalgae; FP-XRF; arsenic; copper; zinc; lead

1. Introduction

With the miniaturisation of x-ray sources, reduction in battery power requirements, and improvements in detector resolution, detection limits and fundamental parameter calibrations, field-portable-x-ray fluorescence (FP-XRF) spectrometry has gained increasing use for the rapid, cost-effective and non-destructive analysis of trace elements in environmental solids over the past two decades (Bosco, 2013). Most publications have described the analysis of dried and sieved or pulverised soils, tailings, dusts and sediments (Radu and Diamond, 2009; Parsons et al., 2013; McComb et al., 2014), with many studies extending the application for screening in situ (Higueras et al., 2012; Weindorf et al., 2012). Recently, means of measuring trace elements by FP-XRF in low density environmental particulates, like paints and plastics, have also been described and tested (Nakashima et al., 2012; Turner et al., 2014; Ytreberg et al., 2015). Because polymers are composed of light elements that are weak absorbers of x-rays, the intensity of characteristic fluorescent x-rays is dependent, in part, on sample thickness (Piorek, 2004). To compensate for low density samples that are thinner than a few mm, therefore, application of a thickness correction algorithm based on measured sample thickness is an important, additional consideration in the fundamental parameter XRF computations (Turner and Solman, 2016).

In the present study, we hypothesize that the XRF approach developed for use on plastics and paints could be applied to the determination of trace elements in marine macroalgae, whose compositional and thickness characteristics bear similarities to those of synthetic polymeric films. Many species of marine macroalgae accumulate trace metals and metalloids from sea water to concentrations several orders of magnitude greater than their environment and serve as potentially useful sentinel organisms of local environmental contamination (Varma et al., 2011; Reis et al., 2014; Malea et al., 2015). While conventional analysis of macroalgae entails digestion of dried material in concentrated mineral acid and subsequent

analysis by, for example, anodic stripping voltammetry, atomic absorption spectrometry or inductively coupled plasma (ICP) spectrometry, the throughput of multiple samples can be time-consuming and labour-intensive. Here, therefore, we investigate the feasibility of a FP-XRF spectrometer (Niton XL3t) calibrated for plastics and with thickness correction capability for the analysis of a variety of trace metals and metalloids in dried samples of a brown (*Fucus serratus*), red (*Palmaria palmata*) and green (*Ulva lactuca*) seaweed. As an independent and comparative measure of the elemental content of the algae, we analyse subsequently digested samples by ICP-mass spectrometry. Although the XRF study is conducted in a bench-top accessory stand, we also discuss the potential for the approach to be employed for in situ monitoring and screening of coastal and estuarine macroalgae.

2. Materials and methods

2.1. Sampling and sample preparation

Individuals of *Fucus serratus*, *Palmaria palmata* and *Ulva lactu*ca were collected at low tide during November 2015 from the intertidal rock pools at Wembury, a protected beach in south Devon, SW England (50º19'03.8"N, 4º05'04.5"W). Samples were transported to the Plymouth University laboratory in zip-locked polyethylene bags where they were washed in a 1:9 solution of ethanol:sea water before surfaces were gently scraped with a polyethylene spatula to remove particulate matter and epiphytes (Gledhill et al., 1998). Different species were then grouped and transferred to ten-litre polyethylene aquaria containing aerated, coastal sea water (salinity ~ 32; pH ~ 8.0) that had been collected in bulk from Plymouth Sound and filtered through 0.6 μm extruded carbon. Samples were acclimated for three to six days under an irradiance of 125 μmol m^{-2} s^{-1} on a 16:8 hour light:dark cycle at 14 $\pm$ 2 ºC.

In a first experiment, three samples of each species were removed from the aquaria and cut into two halves longitudinally. To compare drying method on XRF analysis (through

potential differences in sample integrity, flatness, smoothness and thickness), one half of each sample was oven-dried at 80 ^{o}C for 24 h while the other half was frozen and freeze-dried for 48 h using an Edwards Super Modulyo. These samples are hereafter referred to as 'baseline' and contain ambient concentrations of metals and metalloids.

In a second experiment, 36 one-litre clear polyethylene tanks were filled with filtered sea water. To 27 tanks, one of three concentrations of a combined solution of As, Cu and Zn was added (the rationale for using these elements was based on results from the 'baseline' experiment and as discussed below). Specifically, a stock solution containing $Na_2HAsO_4.7H_2O$, $CuSO_4.5H_2O$ and $ZnSO_4.7H_2O$ (ReagentPlus ®, Sigma-Aldrich) was used to obtain respective concentrations of As, Cu and Zn of 5, 50 and 500 μg L^{-1}, 7.5, 75 and 750 μg L^{-1} and 10, 100 and 1000 μg L^{-1}. Twelve individuals of each species were then allocated to aquaria, with three replicates per treatment that included controls without element addition. After seven days' exposure under the acclimation conditions described above, individuals were removed and cut in half longitudinally, with one half being oven-dried and the other half freeze-dried. These samples, hereafter referred to as 'exposed', were designed to contain a range of elevated concentrations of As, Cu and Zn representative of more contaminated coastal environments.

2.2. FP-XRF analysis

In order to minimise confounding effects arising from differential accumulation of elements by different parts of the macroalgae, sections from the mid-thallus were dissected from each dried sample. Sections were analysed for trace elements (As, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn and Zn) by energy dispersive FP-XRF using a battery-powered, field portable (1.3 kg) Niton XRF analyser (model XL3t 950 He GOLDD+). The instrument employs an x-ray tube with a silver anode operating at up to 50 kV and 200 μA as the source of sample excitation,

and is fitted with a geometrically optimised large area silicon drift detector to detect and register characteristic fluorescent x-rays from the sample.

Elemental concentrations in macroalgal sections were determined using a low density plastics mode by way of a fundamental parameters-based alpha coefficient correction model. Because the intensity of fluorescent x-rays arising from low density materials is affected by the depth of the sample, a thickness correction algorithm, employing a compensation for mass absorption coefficient based on Compton scatter and calibrated down to 0.05 mm, was also applied after sample thickness had been measured with digital callipers.

The XRF was used in the laboratory in a bench-top accessory stand (with the nose pointing upwards) and was connected to a Fujitsu laptop computer via USB and a remote trigger. Samples were placed on to a SpectraCertified Mylar polyester 3.6 μm film which was then positioned such that the smoothest and flattest part of the sample lay directly and centrally above the 8 mm XRF measurement window, a process aided by referring to real-time video footage generated by an integrated CCD camera adjacent to the detector. To increase the effective depth of the thinnest samples (mainly *Ulva*), sections were folded or cut and stacked before being placed above the window. On closing the steel shield of the stand, measurements with appropriate thickness correction were activated through the laptop for a total period of 200 seconds; specifically, counting was performed for 100 seconds each in a low energy range (20 kV and 100 μA) and main energy range (50 kV and 40 μA). Decreasing counting time was found to reduce the number of cases in which elements were detected while increasing counting time (up to 600 seconds) did not significantly increase detectable cases but resulted in a reduction in counting error.

2.3. Macroalgae digestion and analysis by ICP

As an independent and more sensitive measure of the elemental composition of the macroalgae, all baseline (n = 18) and exposed (n = 72) sample sections were subsequently acid-digested and analysed by inductively coupled plasma-mass spectrometry (ICP-MS). Thus, samples of about 0.1 g were accurately weighed into individual Teflon tubes to which 2 ml aliquots of HNO_3 (Fisher Chemical TraceMetal^{TM} Grade) were added. The contents were digested in a CCEM MARS 5 XPRESS microwave at 1600 W for 45 min before being allowed to cool. Digests were then washed into individual 10 ml volumetric flasks and diluted to mark with ultra-pure Millipore Milli-Q water. For an assessment of digestion efficacy and analytical accuracy, a seaweed reference material (*Fucus vesiculosus*, ERM-CD200; certified for As, Cd, Cu, Hg, Pb, Se and Zn) was digested in triplicate likewise.

Seaweed digests were analysed for elements that had been detected by XRF using a collision cell-ICP-MS (Thermo X-series II, Thermoelemental, Winsford, UK) with a concentric glass nebuliser and conical spray chamber. RF power was set at 1400 W and coolant, auxiliary, nebuliser and collision cell gas flows rates were 13 L Ar min^{-1}, 0.70 L Ar min^{-1}, 0.72 L Ar min^{-1} and 3.5 mL 7% H_2 in He min^{-1}, respectively. The instrument was calibrated externally using four standards prepared by dilutions of a QC 26 multi-element solution (CPI International, Amsterdam) in 0.1 M HNO_3, and internally by the addition of 100 μg L^{-1} of In and Ir to all samples and standards. Data were acquired over a dwell period of 10 ms, with 50 sweeps per reading and three replicates.

2.4. Presentation, quality and analysis of data

Spectra arising from the XRF analyses were quantified by fundamental parameter coefficients to yield elemental concentrations on a dry weight basis (in μg g^{-1}) and with a counting error of 2σ (95% confidence) that were downloaded from the instrument to the laptop using Niton data transfer (NDT) PC software. As a performance check of the FP-XRF

in plastics mode, a Niton reference polyethylene disc that had been impregnated with As, Cd, Cr, Hg, Pb, Sb and Se at concentrations up to about 300 μg g^{-1} (PN 180-619, LOT#T-18; diameter = 31 mm, thickness = 13 mm) was analysed in triplicate. Measured concentrations were within 10% of reference values for all elements present with the exception of Pb (15%).

Aqueous concentrations derived from the ICP-MS were converted to dry weight concentrations (in μg g^{-1}) from the volume of diluted digest and mass of macroalga digested. Limits of detection on this basis were < 0.5 μg g^{-1} for all trace elements analysed, and measured concentrations of elements certified in the reference macroalga were within 15% of published values.

Minitab 17 was employed to establish differences in dry weight elemental concentrations arising from the two methods of drying via a non-parametric Wilcoxon signed rank test, and to determine differences in concentrations resulting from addition of elements in the exposed experiments by one-way ANOVA. Correlations and linear regressions establishing relationships between the two analytical approaches were performed in Microsoft Excel 2010.

3. Results

3.1. FP-XRF detection limits

The Niton XLT3t series of FP-XRF analysers calculates element-specific limits of detection (LODs) that are dependent on the characteristics of the sample (e.g. composition and thickness), counting time and mode of instrument application from counting errors multiplied by 1.5 (that is, 2σ x 1.5, or 99.7% confidence interval). Indicative LODs for the three species of seaweed, shown in Table 1, are based on mean counting errors arising from the 200-second analysis of the oven-dried and freeze-dried baseline samples. Among the

algae, LODs are highest for *U. lactuca* and lowest for *F. serratus*, reflecting the sequence of increasing measured thickness and, presumably, primary x-ray absorption and secondary x-ray fluorescence. Among the trace elements, LODs are lowest for As, Cr and Pb and highest for Cd, Ni, Sb and Sn.

Table 1: Mean detection limits (μg g^{-1} dry weight; $n = 6$) of the Niton FP-XRF employed in plastics mode and for a total counting time of 200 s for trace elements in the three species of macroalga.

macroalga	As	Cd	Cr	Cu	Hg	Ni	Pb	Sb	Se	Sn	Zn
F. serratus	3.1	28.8	8.2	11.8	9.8	16.1	4.6	56.8	7.7	37.0	7.9
P. palmata	3.2	31.8	5.7	19.3	14.3	24.8	6.7	66.2	11.8	44.8	12.6
U. lactuca	8.0	44.2	12.5	48.6	35.4	58.9	13.4	87.1	25.4	57.1	23.8

3.2. FP-XRF determination of trace elements in baseline macroalgae

Table 2 summarises the dry weight concentrations of trace elements in the baseline samples as returned by the XRF. (Note that both here and with exposed material, concentrations in the oven- and freeze-dried samples were statistically indistinguishable ($p > 0.05$), despite the latter being flatter, smoother and less curled, and the data for each species of alga have, therefore, been pooled.) Thus, under the operating conditions of the instrument, As was detected in all samples of *F. serratus* and *P. palmata* but in no samples of *U. lactuca*, Cu and Zn were detected in all seaweed species but not always in each replicate, and Pb was only detectable in one or two replicates of each species. Although the XRF occasionally returned concentrations of Cr in *U. lactuca* that were well above the detection limit for the metal, it was subsequently established that this was the result of an analytical artefact related to sample thickness (see explanation below).

Table 2: Number of cases detected and mean and standard deviation of trace element concentrations in baseline macroalgae (μg g^{-1} dry weight) as returned by the Niton FP-XRF in plastics mode and for a total counting time of 200 s.

	As			Cu			Pb			Zn		
macroalga	*n*	mean	sd	*n*	mean	sd	*n*	mean	sd	*n*	mean	sd
F. serratus	6	31.6	5.8	3	18.6	5.9	2	6.6	0.6	6	38.0	11.1
P. palmata	6	7.3	1.8	4	28.4	7.0	1	7.2		4	31.0	24.1
U. lactuca	0			2	42.6	10.2	2	13.4	1.9	6	56.7	16.9

3.3. FP-XRF determination of trace elements in exposed macroalgae

Based on the observations above, individuals of each species were exposed to As, Cu and Zn for a period of seven days in order explore the performance of the XRF over a wider range of trace element concentrations. Note that Pb was not included in the exposures because its fluorescent L_α peak overlaps with the K_α peak of As with the consequence that concentrations of the latter cannot be effectively calculated in the presence of relatively high concentrations of Pb (Parsons et al., 2013). Figure 1 shows the dry weight concentrations of As, Cu and Zn in each algal species returned by the XRF as a function of added aqueous concentration. Here, control concentrations of trace elements in the algae are similar to those determined in the baseline samples and as reported in Table 2. Addition of aqueous As resulted in a non-significant increase in mean concentration in *F. serratus* and *P. palmata* relative to the corresponding controls but only at the highest added concentration for the former species; addition of the metalloid to *U. lactuca*, however, failed to elicit detectable accumulation. Addition of aqueous Cu resulted in significant ($p < 0.05$) increases in mean concentrations relative to the corresponding controls for *P. palmata* and *U. lactuca*, but a significant increase in *F. serratus* was observed only at the highest added concentration of the metal. Addition of aqueous Zn resulted in significant increases in mean concentration

relative to the controls for all species of seaweed, and for *F. serratus* incremental additions of metal were accompanied by successive, significant increases in accumulation.

3.4. A comparison of trace element concentrations returned by FP-XRF and ICP-MS

As an independent and more sensitive method of trace element determination in the macroalgae, all samples analysed by FP-XRF (n = 90) were subsequently digested in concentrated HNO_3 and analysed by ICP-MS. The results revealed no false negatives among the samples and for all elements considered (as listed in Table 1); that is, lack of detection by the XRF was not accompanied by a measurement by ICP that exceeded the corresponding LOD of the XRF. False positives were returned for Cr in all samples of *U. lactuca*; thus, here, the XRF reported concentrations of Cr (up to 100 $\mu g\ g^{-1}$) that greatly exceeded concentrations returned by the ICP (< 1.5 $\mu g\ g^{-1}$). We attribute this discrepancy to the difficulty in obtaining an accurate thickness of the green seaweed and the high sensitivity of Cr determinations to the thickness correction algorithm in the plastics mode of the Niton XL3t (Turner and Solman, 2016).

Direct comparisons of the two approaches for the trace elements detected by XRF (As, Cu, Pb and Zn) are illustrated in Figure 2 and statistical summaries defining the datasets are presented in Table 3. Overall, data points for As are close to and are equally distributed either side of unit slope; for Cu, Pb and Zn, however, most (or all) data points lie above but within an order of magnitude of unit slope. XRF-ICP relationships for all elements displayed a correlation coefficient, r, above 0.8 that was significant ($p < 0.05$), and linear regression analysis revealed lines with slopes, m, when forced through the origin, ranging from about 1 for As to over 2 for Cu and Pb. With respect to individual algal species, all relationships were significant with variation among line slopes except for As in *P. palamata*; here, data

points were clustered around a relatively small range in concentration and a relationship could only be defined with a positive intercept.

Table 3: Statistical definitions of the XRF-ICP relationships shown in Figure 2. Note that all relationships forced through the origin were significant ($p < 0.05$) except for As in *P. palmata* (*m* = slope, *r* = correlation coefficient, ns = not significant).

	As			Cu			Pb			Zn		
macroalga	*n*	*m*	*r*	*n*	*m*	*r*	*n*	*m*	*r*	*n*	*m*	*r*
F. serratus	30	0.959	0.832	25	1.610	0.522	2			30	1.370	0.959
P. palmata	25	1.052	0.108 (ns)	28	1.630	0.335	1			27	1.650	0.909
U. lactuca	0			26	2.360	0.792	2			27	2.690	0.887
all	55	0.962	0.956	79	2.260	0.893	5	2.443	0.849	84	1.690	0.827

4. Discussion

Although more sensitive, conventional (laboratory-based) XRF techniques have been employed to determine trace elements in seaweeds and other biological materials after complete sample digestion or chemical treatment-pelletisation (Vlachos et al., 1998; Ferreira et al., 2012; McComb et al., 2014), the present study appears to be the first to report the direct application of a field-portable instrument in this respect. Advantages of a portable instrument that incorporate a low density mode and when used in a laboratory accessory stand include minimal sample preparation (e.g. cleaning and drying), non-destruction of material, rapid, multi-element analysis, avoidance of hazardous waste generation and minimal operator training.

The Niton XL3t FP-XRF configured in a plastics mode and with thickness correction is able to detect a number of elements in various species of algae collected from a protected coastal site down to dry weight concentrations of a few $\mu g\ g^{-1}$. That overall and species-specific relationships between XRF and ICP are, in all but one case, significant, indicates the counts from the FP-XRF analysis are converted via fundamental parameters into concentrations that

289 are directly proportional to those returned by the independent digestion-ICP approach. In the
290 case of As, an overall slope close to unit value suggests that the plastics mode of the Niton
291 XL3t instrument is suitable for direct determinations in macroalgae. Where slopes exceed
292 unit value and the XRF over-estimates elemental concentrations, however, data require
293 empirical adjustment. This may be achieved by applying element- and, perhaps, algal-
294 specific corrections to measurements obtained by the XRF. Alternatively, the instrument
295 allows the operator to edit and store up to four alternative calibrations per mode for a suite of
296 elements by adding slopes and, if necessary, intercepts to both main and low energy ranges.
297 Because of the significant proportionality between concentrations returned by the FP-XRF
298 and those delivered by an independent method whose accuracy has been verified, the method
299 meets US EPA validation guidelines; specifically, As analyses meet the definitive level
300 criterion ($r > 0.9$) and Cu, Pb and Zn the quantitative screening level criterion ($r > 0.7$)
301 (Environmental Protection Agency, 2007).
302
303 The portable XRF also has potential for the direct monitoring of the spatial and temporal
304 distribution of trace elements in macroalgae in situ. Here, implementation of additional
305 safety features would be necessary, such as a back scatter radiation shield or a portable test
306 stand. Field measurements would require suitable water protection of the detector window
307 and would entail analysing samples without drying and stacking but after appropriate
308 cleaning and thickness measurement. Sensitivity, error and, possibly, accuracy would be
309 compromised by the presence of water through its contribution to density and its propensity
310 to scatter and photoelectrically absorb radiation (Parsons et al., 2013). Algal water content
311 would also have to be factored in for dry weight concentrations to be determined through
312 element- and species-specific wet-to-dry weight algorithms, although it is possible that
313 measurements of Cl in the low energy range (K_α = 2.62 keV, K_β = 2.82 keV) could be used

as a proxy for sea water content (Tjallingii et al., 2007). The feasibility of in situ screening for trace elements in a variety of coastal macroalgae is currently being investigated.

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Figure 1: Dry weight concentrations of As, Cu and Zn in *Fucus serratus* (hatched), *Palmaria palmata* (stippled) and *Ulva lactuca* (zig-zag) as returned by the Niton FP-XRF and following aqueous addition of different concentrations of each trace element. Note that errors denote one standard deviation about the mean of up to six independent determinations, and that As was never detected in *U. lactuca*.

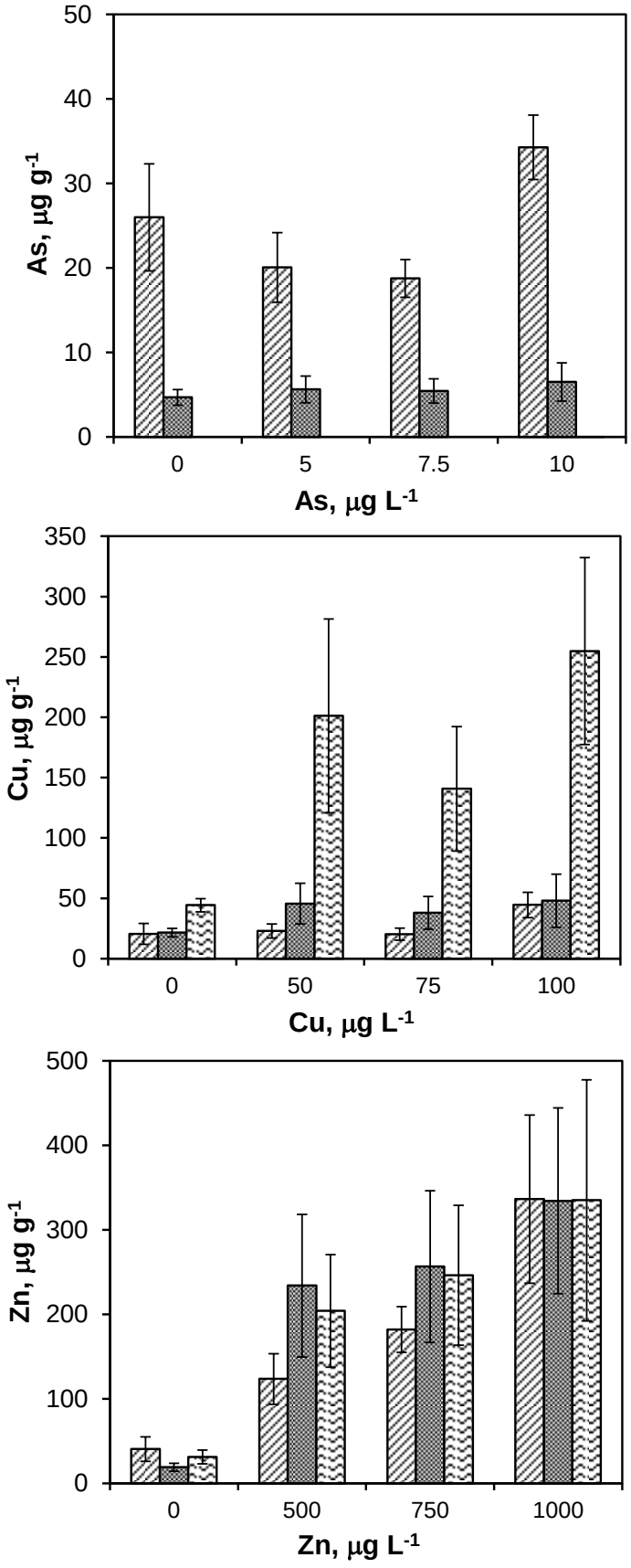

Figure 2: A comparison of dry weight concentrations of As, Cu, Pb and Zn in *Fucus serratus* (X), *Palmaria palmata* (▲) and *Ulva lactuca* (o) returned by the Niton FP-XRF and by ICP-MS following acid digestion. Statistical parameters defining each dataset are given in Table 3 and solid lines denote unit slope.